THE PHYSICO-CHEMICAL PROPERTIES OF STEEL.

Charles Griffin & Co., Limited, Publishers.

Sixth Edition, Thoroughly Revised Throughout. Profusely Illustrated. Large 8vo
Two Volumes. In all 1000 pages. Cloth. 42s. net.

With Additional Chapter on The Electric Smelting of Steel.

THE METALLURGY OF STEEL.

By F. W. HARBORD, Assoc.R.S.M., F.I.C., and J. W. HALL, A.M.Inst.C.E.

Vol. I.—Metallurgy. Vol. II.—Mechanical Treatment.

The *Engineer* says, at the conclusion of a review of this book:—"We cannot conclude without earnestly recommending all who may be interested as makers or users of steel, which practically means the whole of the engineering profession, to make themselves acquainted with it as speedily as possible."

Fifth Edition, Revised and Enlarged. Pp. i-xv + 486. With 130 Illustrations 18s. net.

THE METALLURGY OF IRON.

By THOMAS TURNER, Assoc.R.S.M., F.I.C.,
Professor of Metallurgy in the University of Birmingham.

"A thoroughly useful book, which brings the subject up to date. Of great value to those engaged in the iron industry."—*Mining Journal.*

Second Edition. In Medium 8vo. Cloth. Pp. i-xiii + 249. With Frontispiece and 164 Illustrations, including many Photo-Micrographs. 12s. 6d. net.

CAST IRON
IN THE LIGHT OF RECENT RESEARCH.

By W. H. HATFIELD, D.Sc., B.Met., A.M.I.Mech.E.

"A valuable addition to Griffin's noted metallurgical publications."—*Mining Magazine.*

[illegible]

Third Edition. Thoroughly Revised. In Medium 8vo. Pp. i-vii + 384. With Illustrations. 18s. net

GENERAL FOUNDRY PRACTICE:
A Practical Handbook for Iron, Steel and Brass Founders, Metallurgists, and Students of Metallurgy.

By A. McWILLIAM, A.R.S.M., and PERCY LONGMUIR.

"The student of foundry work . . . needs no other text-book. . . . The book contains a tremendous amount of information, and is well written."—*Engineering Times.*

Third Edition, Revised and Enlarged. Frontispiece in Colours, and Beautiful Series of Photo-Micrographs. Pp. i-xix + 332. 15s. net.

ALLOYS
AND THEIR INDUSTRIAL APPLICATIONS.

By EDWARD F. LAW, A.R.S.M.

"In every way worthy to take is place in the Series . . . the current text-book for students of a fascinating and indispensable subject."—*Mining Journal.*

Second Edition, Thoroughly Revised. Pp. i xvii + 313. With 195 Photo-Micrographs, Diagrams, and Figures. 10s. 6d. net.

THE MICROSCOPIC ANALYSIS OF METALS.

By FLORIS OSMOND and J. E. STEAD, D.Met., F.R.S.
Revised and Corrected by L. P. SYDNEY.

"The subject is treated in a masterly manner . . . altogether the new edition should prove invaluable to metallurgists."—*Mining World.*

"Of all the books which have dealt with this subject in its many aspects, surely this one remains supreme."—*Chemical World.*

LONDON: CHARLES GRIFFIN & CO, LTD., EXETER STREET, STRAND, W.C.2.

THE
PHYSICO-CHEMICAL PROPERTI
OF
STEEL.

BY

C. A. EDWARDS, D.Sc.,

PROFESSOR OF METALLURGY, MANCHESTER UNIVERSITY

SECOND EDITION, THOROUGHLY REVISED.

With 218 Illustrations, including 6 Folders.

LONDON:
CHARLES GRIFFIN & COMPANY, LIMIT
EXETER STREET, STRAND, W.C. 2.
1920.

[*All Rights Reserved.*]

PROPERTY OF
CARNEGIE INSTITUTE OF TECHNOLOGY

PREFACE TO SECOND EDITION.

In this edition, which was required at an earlier date than the author anticipated, the introductory section dealing with special steels has been rewritten and enlarged. A considerable number of new facts have been included in the chapters on chromium steels and high-speed steels.

There is an additional chapter dealing with some of the more important methods of making hardness tests, and the relationship between these are discussed. The connection between Brinell hardness and other physical properties are also dealt with.

In another new chapter the influence of constitution on electrical resistivity is discussed with special reference to iron and steel.

C. A. EDWARDS.

Manchester, *March*, *1920.*

PREFACE.

THE object of the present book has been to give a comprehensive account of the chemical and structural constitution of steels; to describe the internal changes that occur when steels are heated and cooled under varying conditions, and to indicate the effects of these changes upon the properties of the materials. Considerable attention has been given to the thermal and structural transformations of the iron-carbon system, because they are the fundamental elements of all steels. This has been treated in the manner which is now being generally adopted for metallic alloys—namely, from the point of view of the equilibrium diagram—and the subject is developed upon this foundation. An effort has been made to gather all the important facts dealing with the metallography of steel and present them in a condensed form. Hence, although it is not a large volume, the author ventures to hope that it will, on that account, be more appreciated by students of Metallurgy and Engineering. The fact that very complete references are given to all the early and important recent literature should make the present treatise useful even to those who have specialised in this branch of Metallurgy.

The author very gratefully acknowledges the valuable help he has obtained from the many publications by Professor Arnold, Sir Robert Hadfield, Mon. F. Osmond, Dr. Stead and others, to whom Metallurgists and Metallurgical Engineers owe so much. They have placed the study of steel upon a sound scientific basis and demonstrated how the knowledge thus acquired can be advantageously applied in the workshops.

The author would like to express his thanks to Mr. J. H. T. Tudsbery, Secretary of the Institution of Civil Engineers; to Mr.

Edgar Worthington, Secretary of the Institution of Mechani
Engineers; Mr. G. Shaw-Scott, Secretary of the Institute of Meta
and especially to Mr. G. C. Lloyd, Secretary of the Iron and St
Institute, for their ready permission to make extracts and use ma
illustrations from the Proceedings of the respective Societies.

CHARLES A. EDWARDS

MANCHESTER, *March, 1916.*

CONTENTS.

CHAPTER I.

CONSTITUTION OF METALLIC SYSTEMS.

Allotropy—Effect of Impurities on Allotropic Transformations—Phase Rule—Constituents in Metallic Alloys—Thermal Critical Points and Ranges—Freezing Point Curves—Equilibrium Diagrams of Binary and Ternary Systems, ...

CHAPTER II.

STRUCTURE OF METALS.

Structural Components: Crystals—Preparation of Microsections—Amorphous Phase at Crystal Boundaries—Twin Crystals formed on Annealing—Twin Crystals produced by Mechanical Strain—Slip Bands, ...

CHAPTER III.

IRON.

Recalescence—Critical Points in Iron—Alpha, Beta, and Gamma Iron—Magnetic and Electrical Properties—Specific Heats—Structure—Recrystallisation—Strength at Varying Temperatures, ...

CHAPTER IV.

CONSTITUTION OF THE IRON-CARBON SYSTEM.

Equilibrium Diagrams—Carbide of Iron—Critical Points and Ranges—Solidification and Changes on Cooling, ...

CHAPTER V.

MICRO-STRUCTURE OF IRON-CARBON STEELS.

Constitution of Annealed Steels—Ferrite, Cementite, Pearlite, and Sorbitic Pearlite—Quenched Steels—Austenite, Martensite, and Troostite—Effect of Quenching on Critical Points—Crystal Twinning Produced by Quenching—Relative Hardness of Constituents in Steel, ...

CHAPTER VI.

SOLIDIFICATION OF STEEL INGOTS.

PAGES

Freezing of Simple Liquids—Segregation—Blowholes—Position of Pipe and Blowholes in Steel Ingots—Blowhole Segregation—Fluid Compression, . 79-94

CHAPTER VII.

IRON-CARBON STEELS.

Mechanical Properties of Annealed and Rolled Bars—Effect of Heat-treatment—Mechanical Properties of the Different Types of Pearlite—Chemical Composition and Tensile Strength, ... 95-103

CHAPTER VIII.

PHOSPHORUS.

Iron-Phosphorus Compounds—Equilibrium Diagram—Carbon and Solubility of Phosphorus, ... 104-109

CHAPTER IX.

SULPHUR.

Red-Shortness—Manganese Sulphide—Ferrous Sulphide—Sulphur Prints—Ferrous and Manganese Sulphide Diagram, ... 110-116

CHAPTER X.

BURNING AND OVERHEATING OF STEEL.

Definitions of—Crystal Growth at High Temperatures—Effect of Overheating and Burning on the Properties of Steel—Refining of Overheated and Burned Steel—Annealing of Steel Castings, ... 117-124

CHAPTER XI.

DEFORMATION AND STRAIN-HARDENING OF METALS.

Plastic Deformation—Theory of Hardening by Cold Work—Amorphous Phase in Metals—Rapid Recrystallisation of Iron and Mild Steel after Deformation, ... 125-133

CHAPTER XII.

THE PROPERTIES OF COLD-DRAWN WIRE AND THE EFFECT OF ACID CLEANING.

Carbon and the Amount of Cold Work Steel can Support without Breaking—Volume and Hardness—Annealing Temperature—Galvanising—Acid Cleaning—Effect of Hydrogen, ... 134-140

CHAPTER XIII.

CEMENTATION AND CASE-HARDENING.

PAGES

Carburising—Refining—Hardening—Use of Nickel, ... 141-144

CHAPTER XIV.

METHODS OF TESTING HARDNESS.

Brinell Test—Ludwik Test—Influence of Load—Influence of Time—Dynamic Indentation Test—Dynamic Indentation and Elastic Rebound—Ultimate Stress and Brinell Hardness—Molecular Attraction and Hardness, . . 145-163

CHAPTER XV.

THEORIES OF HARDENING BY QUENCHING.

Action of Quenching—Lowering of Carbide Change—Suppression of Carbide Change—Allotropic Theory—Fineness of Structure—Amorphous Phase—Crystal Twinning—Interstrain, ... 164-178

CHAPTER XVI.

SPECIAL STEELS.

Object of Using Special Elements in Steel—Influence of Initial Temperature and Rate of Cooling—Special Elements and Depth of Penetration of Quenching—Nickel—Iron Alloys—Nickel-Iron-Carbon Alloys—Their Critical Points and Properties, ... 179-208

CHAPTER XVII.

TUNGSTEN-CARBON STEELS.

Effect of Tungsten upon the Critical Points of Steel—Influence of Initial Temperature—Constitution, ... 209-212

CHAPTER XVIII.

HIGH-SPEED TOOL STEELS.

Development and Use of High-Speed Steels—Composition and Cutting Properties of Different Types of Tool Steel—Hardening—Secondary Hardening—Influence of Chromium and Tungsten—Cooling Curves—Theories—Microstructures, ... 213-226

CHAPTER XIX.

MANGANESE.

Chemical Constitution of Manganese Steels—Critical Points—Mechanical Properties, ... 227-233

CHAPTER XX.

CHROMIUM.

PAGE

Chemical Constitution of Chromium Steels—Cooling Curves—Critical Cooling Rates—Influence of Composition on Critical Cooling Rates—Mechanical Properties, ... 234-24

CHAPTER XXI.

Aluminium, Silicon, and Vanadium Steels, ... 246-25

CHAPTER XXII.

Structural Constitution of Special Ternary Steels, ... 253-258

CHAPTER XXIII.

ELECTRICAL CONDUCTIVITY AND CONSTITUTION.

Influence of Constitution of Alloys upon Electrical Conductivity—Electrical Resistance of Iron—Effect of Elevated Temperatures on Resistivity of Iron—Formula for Calculating the Resistance of Steel from its Chemical Composition—Quenching Temperature and Resistance of Carbon Steels, . . 259-27

Index to Authors Cited, ... 275-27

Index to Subjects, ... 279-28

THE PHYSICO-CHEMICAL PROPERTIES OF STEEL.

CHAPTER I.

CONSTITUTION OF METALLIC SYSTEMS.

Allotropy.—It is well known that the properties of matter are to a very large extent governed by temperature, and that, within certain limits, changes in temperature involve changes in the general properties of both simple and compound substances, and in many cases may cause an actual alteration in the physical state. The liquefaction of a solid or the gasification of a liquid, which are accompanied by pronounced changes in the properties of the substance, are examples of this. In addition to these changes it also frequently happens that both in metallic and non-metallic elements and compounds totally different chemical, physical, and mechanical properties are assumed, without any change of state or chemical composition, at a certain well-defined temperature. When such transformations occur in a substance they are described as due to allotropy, and the temperature at which the change occurs is referred to as the critical point. On passing through that temperature the mass is said to undergo an allotropic transformation, and the less common variety is termed the allotropic modification or the allotrope of the substance or element concerned. Allotropic changes are brought about by some unknown and so far indeterminable internal atomic or molecular re-arrangement of the mass which is accompanied by a change in the crystallographic habit of the element.

An allotropic transformation is almost invariably accompanied by a thermal disturbance, which takes the form of an absorption of heat if the change occurs whilst the temperature of the specimen is being raised, and of an evolution of heat if it occurs whilst the temperature of the specimen is being cooled.

In this respect the thermal characteristics of allotropic changes are exactly analogous to the absorption of heat which occurs when a body passes from the solid to the liquid, and from the liquid to the gaseous state, and the evolution of heat which takes place when these changes occur in the reverse direction.

The discontinuities in the thermal properties of an element can be readily detected by making careful observations of the manner in which the element absorbs or emits heat on being heated or cooled. If a thermal transformation of this kind be known to occur in an absolutely pure element, it is generally considered that at that particular temperature the element passes from one allotropic state into another. As a rule, however, at the same temperature as the thermal change, a similar discontinuity is evident in many properties of the substance. A rather doubtful factor in this connection, and one which it is often difficult to determine, is the effect of small quantities of impurities. Exceedingly small traces of impurities might have the effect of producing many of the characteristic features of an allotropic change in an element which, when really pure, would give no such phenomena. In view of this, it is important to remember that in some cases changes which are now regarded as being due to allotropy may ultimately be found to be caused by the presence of a small quantity of another element. This uncertainty makes it necessary to be somewhat cautious in using the term allotropy, but if a definite critical point is observed in an element which has been obtained in the purest possible condition, that critical point may be regarded as being caused by an allotropic change, though future investigation might render such a view untenable.

The effect of impurities or added elements upon the temperature at which an actual allotropic change occurs is similar to the effect of salts upon the freezing point of water—*i.e.*, if the foreign elements are soluble they may raise or lower the temperature at which the change would normally take place. The temperature of the change is lowered by the addition of an element more soluble in the modification that is stable at the higher than in the one that exists at the lower temperatures; the effect is in the reverse direction if the added element be more soluble in the modification that persists at the lower temperatures. Examples of all these phenomenal changes are encountered in the domain of the practical preparation and manufacture of metallic alloys, and each type is found in steels. Since, therefore, the properties of elements may undergo such remarkably sudden transformations at certain critical temperatures, and as the presence of foreign elements may have a very marked effect upon the temperatures at which such changes occur, it will be seen how important it is to know the temperature of each change in elementary bodies, and the exact influence accidental impurities as well as intentional additions have upon those critical points. The necessity of experimental data and research along these lines becomes the more evident when it is remembered that even compound bodies that are perfectly homogeneous at one temperature may be decomposed into a heterogeneous mass of two or more constituents which possess totally different properties.

The physico-chemical law known as the "Phase Rule" has proved exceedingly useful in the study of metallic alloys. Whilst it is unnecessary to give a detailed description of this law, it is now so widely used and so frequently introduced into the discussions on the constitution of steel, that some knowledge of its application is now almost indispensable to students of this interesting subject. Shorn of many of its more theoretical details, the phase rule is really simple, and may indeed be regarded as a common-sense law so far as metallic systems are concerned. The essential features of this law will be described later, because they will be more fully appreciated after discussing the various constituents which may exist in alloys, and the methods of graphically illustrating the ranges of temperature and composition over which they may exist.

Constituents in Metallic Alloys.—The constituents which are known to be capable of existing in metallic alloys are :—

1. An alloy may consist of an intimate mixture of its constituents distributed throughout the mass in a perfectly pure condition.
2. The elements contained in an alloy may be capable of existing in different allotropic modifications.
3. Two or more of the elements in an alloy may be mutually soluble in each other, even when they are in the solid state, in which case they give rise to what is known as crystalline solid solutions. A solid solution is a homogeneous mixture of two or more substances in the solid condition. Metallic solid solutions are solid isomorphous mixtures.
4. Intermetallic compounds are often present in alloys, and may be formed by the combination of two metals, or by the union of a metal with a non-metallic element, such as carbon and sulphur, etc.
5. Eutectics, which are frequently described as constituents, are really intimate mixtures of two or more constituents which have crystallised from the liquid at the same time. During solidification the solid eutectic does not undergo any change in composition, and the composition of the liquid also remains the same during freezing. They possess the lowest melting point of any mixtures of their constituents.
6. Eutectoids consist of two or more constituents which have been simultaneously deposited from a homogeneous solid solution of the same composition. They are similar to eutectics in structure, etc., but are formed whilst the mass is completely solid.

Thermal Critical Points and Ranges.—If the rate at which a cooling mass of any substance which undergoes no physico-chemical change be observed, it is found that the rate of cooling has a constant incremental variation. There is no sudden variation in the rate at which it parts with its heat. Hence, if temperature observations are taken per unit of time, and these are plotted as vertical ordinates, whilst the times are plotted as horizontal ordinates, a perfectly continuous curve of the kind shown in A, fig. 1, is obtained. Since the actual rate at which the mass loses its heat decreases as its temperature approaches that of the surrounding atmosphere, the curve which is obtained is parabolic, and not a straight one.

When similar data are taken, and plotted in the same manner, for the cooling of a pure liquid metal B, fig. 1, illustrates the type of curve which is obtained. In this case the fall of temperature is progressive, and the curve smooth so long as the metal remains in the liquid condition, but the moment the mass begins to solidify the cooling is arrested and the temperature remains constant until the whole of the metal has passed from the liquid to the solid state. Afterwards the temperature again begins to fall, and tends to attain the previous rate of cooling. The solidification is, therefore, represented on the curve by the line *ab*. The arrest in the cooling is caused by the crystals that are formed, giving out their latent heat of fusion, which under normal conditions is sufficient to counteract the l of heat by radiation and conduction, etc. The process of crystallisat automatically maintains a constant temperature, until the last drop of liq is transformed into solid crystals.

If the rate of cooling be abnormally rapid and the liquid be undisturb it is possible for the temperature of the mass to fall a few degrees bel the freezing point without the separation of any crystals. The term wh is generally used to describe this kind of supercooling is "surfusion." Sup cooling often leads to recalescence, which is due to the sudden liberat of heat, which causes the temperature of the mass to be raised. In met the possible extent of surfusion is limited to a few degrees, because of th high rate, and facility, of crystallisation from the liquid state. A temperatu is soon reached at which the liquid condition can no longer persist, and relatively large quantity of the mass solidifies quite suddenly, with t result that sufficient heat is evolved to raise the temperature to that of t normal freezing point. The curve which is obtained under these conditio is shown in C, fig. 1, where the degree of surfusion is represented by t line *ab*, and the true freezing point by *bc*. It ought perhaps to be mention at this stage that in many cases solid alloys can be supercooled to man hundred degrees Centigrade below that at which it would normally underg a transformation. Quite a different type of curve is obtained from the da which is taken for the majority of alloys. As a rule, the mixture remai liquid at a lower temperature than one of its constituents, and frequent lower than both. Further, when solidification sets in, the fall of temperatu is not suddenly arrested, but merely retarded at first (*a*) followed at a low temperature by a complete arrest (*bc*), curve D, fig. 1.

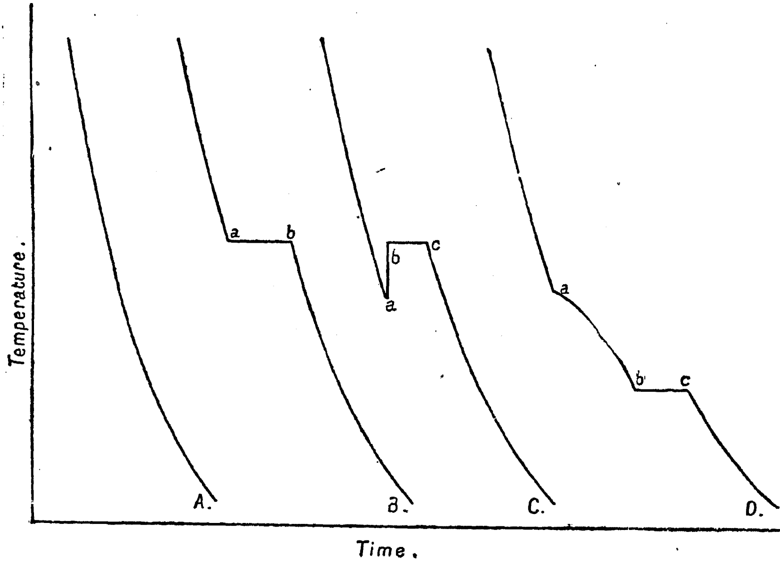


Fig. 1.

The lowering of the freezing point of a pure metal by the addition of another is due to what is known as the osmotic solution pressure. The temperature at which the molecules can become marshalled into a crystalline order is lowered by the pressure which is thus brought to bear. As will be noticed from the character of the cooling curve D, the solidification process is different from that of a pure metal. If the cooling curves of the whole series of alloys consisting of the two metals A and B be determined, they will clearly indicate that the temperature at which the liquid mixtures begin to freeze is governed by the amount of the added metal contained in them. Thus the initial freezing point of the pure metal A, fig. 2, is progressively lowered by increasing additions of B, and a similar effect is produced by adding A to B. By plotting these temperatures as vertical ordinates and the percentage composition as horizontal ordinates, a diagram is obtained which indicates the temperatures at which the various mixtures begin to solidify. The lines *a*, *b*, *c*, fig. 2, thus obtained are known as the liquidus lines, and represent the temperatures just above which the alloys are perfectly liquid. The solidus D *b* E is obtained by drawing a line through the temperatures at which the last trace of liquid is transformed into solid.

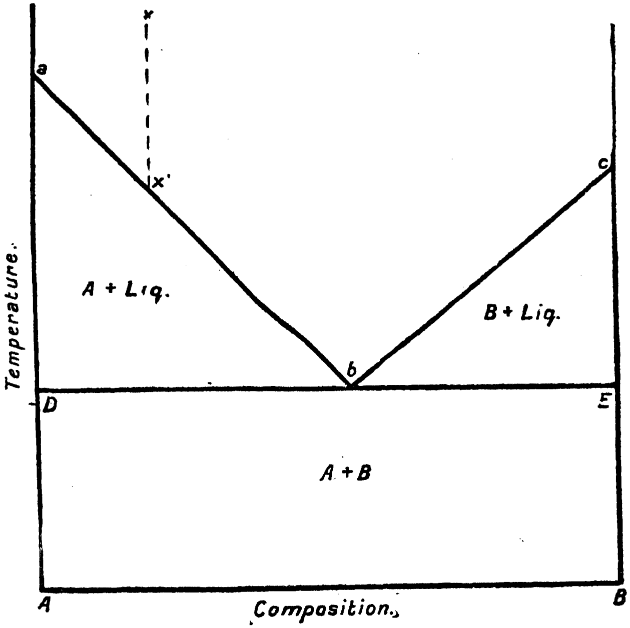


Fig. 2.

In this way an equilibrium diagram is produced, which in this case represents the various areas of temperature and composition within which the phases or constituents, liquid, A + liquid, B + liquid, and A + B may exist in a stable condition.

If, therefore, we consider an alloy of the composition x, fig. 2, it is obvious that on cooling the liquid there will be a retardation in the rate of cooling at the temperature x', which is due to the separation of a certain number of crystals of the pure metal A. As a result of this separation the relative amount of the metal B left in the remaining liquid is increased, and its freezing point or the temperature at which it is capable of depositing a further quantity of crystals is consequently lowered. This process of selective separation of the metal A and enrichment of the residual liquid, in the relative amount of the metal B it contains, proceeds as the temperature falls, until the temperature of the line D *b* E is reached. At this temperature the composition of the remaining liquid corresponds with the eutectic mixture *b*, and it solidifies at a constant temperature—*i.e.*, crystals of A and B are deposited alongside of each other. With mixtures that fall to the right of the eutectic point *b*, the metal B is the first to separate from the liquid, but in all cases when the temperature D *b* E is reached the composition of the liquid corresponds to the eutectic alloy *b*.

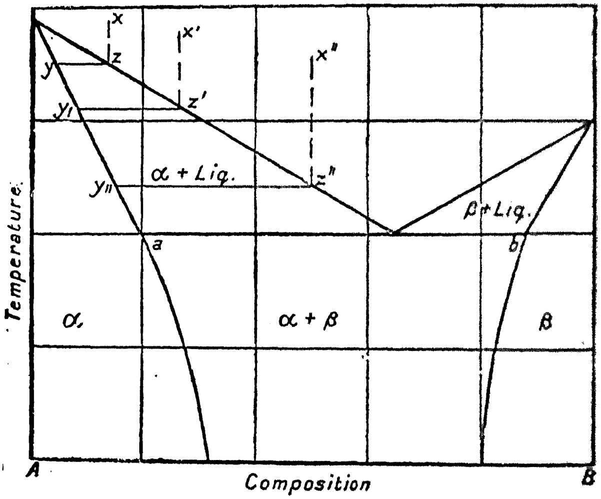


Fig. 3.

In many cases of alloys the solid which separates from liquid mixtures is not one of the pure constituents, but a solid homogeneous solution of the two. Under these conditions the solid which is deposited and the remaining liquid are changing in composition during the whole period of solidification. Fig. 3 represents the equilibrium diagram of a series of this kind. The necessity for the solid crystals that are first formed to change in composition during the freezing period will, no doubt, be readily understood after considering the following facts:—In the case of the three alloys, x, x', and x'', they each begin to solidify at the respective temperatures z, z', and z''. The solid crystals, which are then deposited, and which are in true equilibrium with the liquids, correspond in composition with the points y, y', y''. Therefore, during the solidification period the liquid is constantly changing in composition, and as any given liquid can have only one set of crystals in equilibrium with it, those which have been previously formed from pre-existing liquids must adapt themselves as regards composition to the new conditions. Hence their composition is changed by a process of diffusion.

Fig. 4 represents the diagram of a series, in which an intermetallic compound, A_xB_y, is formed. This series need not be considered in detail, because it may be taken as representing a combination of the two types previously referred to.

In addition to the changes that occur during solidification, many alloys are capable of undergoing marked transformations in structural constitution, which are accompanied by corresponding alterations in mechanical properties, at certain well-defined critical temperatures, even when the mass is completely solid. These changes are perhaps the most important that metallurgists have to consider, because it is largely owing to their existence that the properties of alloys can be modified to suit so many requirements simply by subjecting them to judicious heat-treatment.

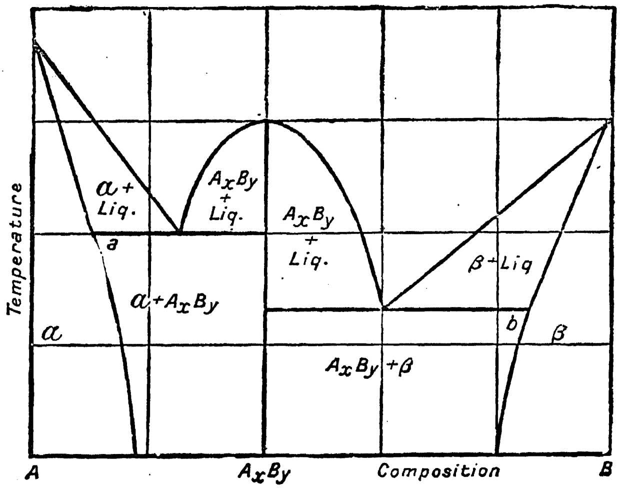


Fig. 4.

Typical examples of transformations in the solid state are illustrated in figs. 5 and 6. In fig. 5 the pure metal A is represented as passing from one allotropic condition β into another α at the temperature *a*.

The β variety is capable of holding a certain quantity of the added element B in solid solution, but no such solution is possible with the α variety. The area *a*, *b*, *c* indicates the stable range of the β solid solution, from which it will be seen that the extent of solution is largely governed by the temperature. As the percentage of the element B is raised from *d* to *b*, it lowers the temperature at which the α modification is formed; this is shown by the sloping line *a*, *b*. It should be noted that the whole of the mass is not changed bodily into α at the temperatures *a*, *b*, but a process of selective separation takes place with falling temperature, which is similar to that previously considered for the solidification of alloys. With mixtures containing more than *b* per cent. of B, the solid solutions deposit the pure metal B at temperatures on the line *b*, *c*. In all cases when the temperature *d*, *b*, *e* is reached there is a certain amount of the eutectoid *b* present, which then transforms bodily into crystals of *α* and B, in the same manner as liquid eutectics deposit crystals of their constituents.

From what has been said above, the changes represented in the diagram, fig. 6, will be understood, the only differences being that in this series no allotropic change takes place, and that one of the constituents which crystallises from the *β* solid solution is not a pure metal, but another kind of solid solution—viz., *a*, which is capable of dissolving increasing quantities of the metal X, as the temperature is lowered.

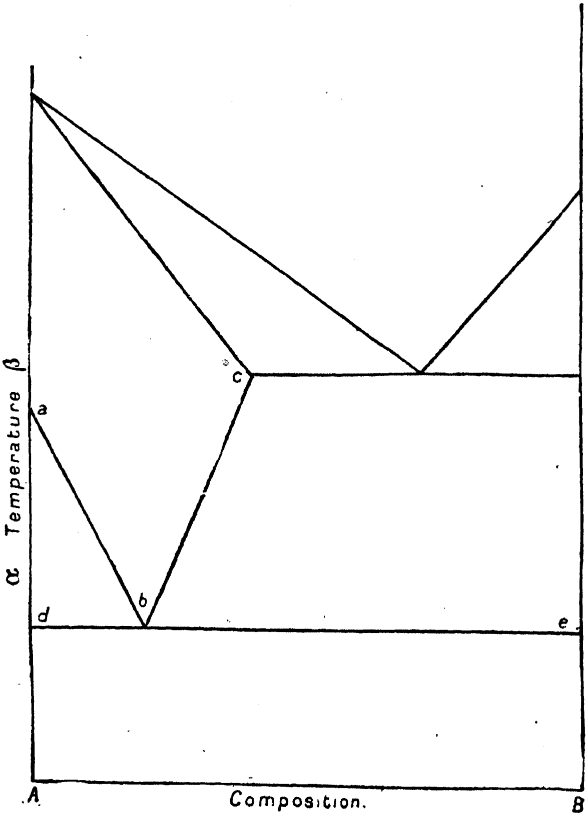


Fig. 5.

Considering that most commercial alloys contain more than two elements, it is of some practical importance to describe some of the changes which occur in ternary mixtures. Accordingly, the following brief account is included:—

Ternary Alloys.—The simplest way of representing graphical ternary series of alloys is by means of an equilateral triangle. Each co of the triangle represents a pure metal. The three sides of the trian fig. 7, correspond with the three binary mixtures A + B, B + C, and C + and any point inside the triangle indicates a certain alloy of the three me From any point on the vertical lines drawn from each base to meet

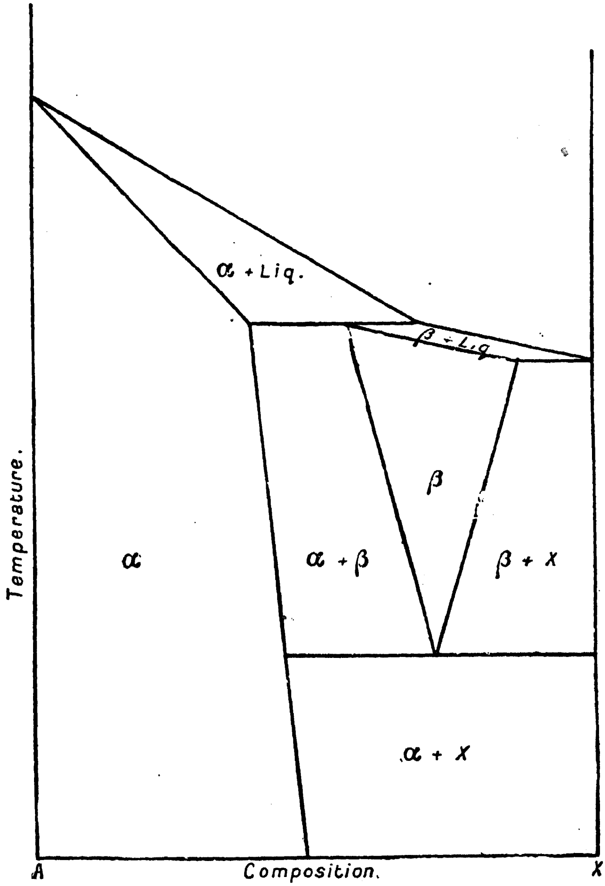


Fig. 6.

corresponding corners, the percentage of each metal present can be re determined by measuring the distance from the point to the base: the centage of the metal represented by the corners opposite is the dist so found expressed in percentages of the total height of the triangle. sequently the length of the lines drawn from any point in the triang meet the three sides at right angles is proportional to the percentag each metal represented by the corner towards which the line tends, and sum of the length of the lines so drawn is equal to the height of the triangle. For example, if it is desired to determine the percentages of A, B, and C in an alloy represented by the point *a*, fig. 7, the amount of A present is proportional with the line *a*, *e*; B with the line *a*, *e′*, and C with the line *a*, *e″*. Alloys occurring upon lines drawn from the sides of the diagram to the corresponding apex, have two of the components relatively constant while the third varies. A line drawn parallel with one of the sides of the triangle represents a series of alloys in which the percentage of one of the components is constant. The temperatures at which the liquid alloys begin to solidify on cooling—*i.e.*, the liquidus—are represented by drawing lines through identical freezing points, and thus obtaining isothermal lines for the whole series.

With the triangular diagram it is only possible to indicate variations of composition. To represent temperature a new axis is taken perpendicular to the plane of the triangle. Thus when temperature and concentration are considered together, it is necessary to have a right triangular prism.

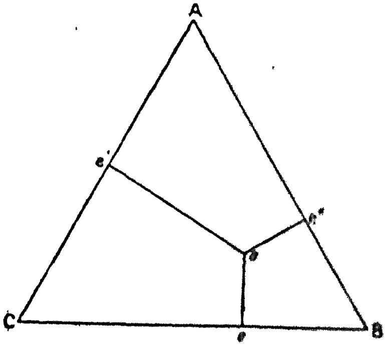


Fig. 7.

The upper or liquidus surface of such a figure is always irregular, and indicates the temperature at which the various alloys begin to deposit solid. It is much more difficult to illustrate the solidus, and the structural and other changes occurring below the solidus, for it is necessary to cut the model into sections, each of which corresponds with a group of alloys possessing the same physical constitution within the limits of the temperature represented by the section.

A projection of such a sectional model showing the constitution of a hypothetical ternary system of the simplest type is shown in fig. 8. In this case the three metals A, B, and C are mutually soluble in each other when in the liquid state, but insoluble when the alloys are just solid. Each binary system gives rise to one eutectic—viz., A + B, eutectic *e*, B + C, eutectic *e′*, and C + A, eutectic *e″*—and from these three the ternary eutectic *e* is formed. To show correctly by means of a solid model, the changes of constitution through which these alloys pass on cooling from the liquid condition, down to temperatures below which the ternary eutectic solidifies, necessitates having the model in seven sections. An easier and perhaps more comprehensive method is to use for different temperatures triangles which are divided into areas showing the boundaries of the phases that are present at those temperatures. The constitution of a system like A, B, C, fig. 8, can then be indicated by means of the three diagrams, figs. 9, 10, and 11. Following the process of freezing for the group of alloys which fall in the area A $x\,y\,z$, fig. 9, these mixtures on cooling begin to solidify with the deposition of crystals of the pure metal A, and the composition of the mother

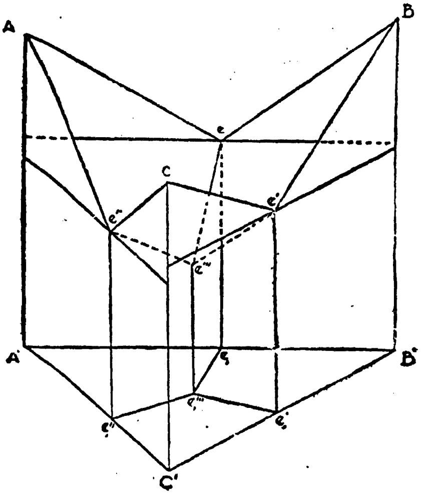


Fig. 8.

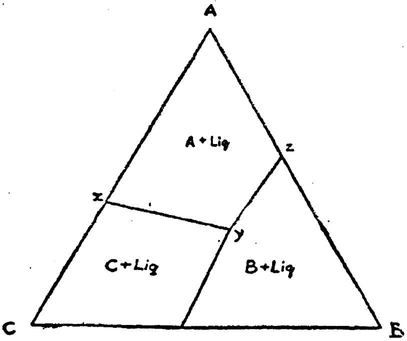


Fig. 9.

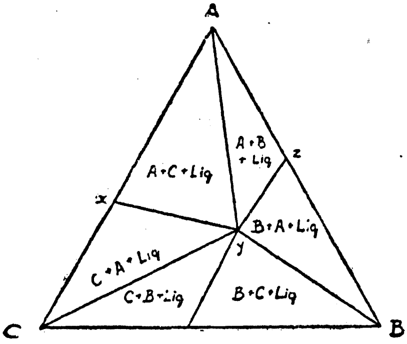


Fig. 10.

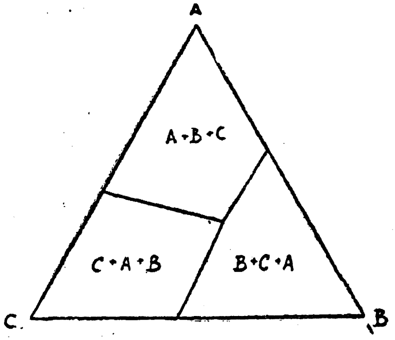


Fig. 11.

liquor is thereby altered. The second period of solidification depends upon the particular side of A y (fig. 10) that the original composition of the alloy happens to place it. With alloys to the right of the line A y the composition of the mother liquor gradually approaches a point on the line $y\,z$ when the binary eutectic z begins to separate: in the secondary period of freezing of alloys on the left of the line A y the binary eutectic x separates from the liquid. In both cases the composition of the mother liquor ultimately corresponds to the ternary eutectic *y*, and then solidifies at a constant temperature, with the simultaneous deposition of A, B, and C. Alloys which are represented by points upon the line deposit the pure metal A, and the composition of the liquid gradually changes until it reaches that of the ternary eutectic, without the intermediate separation of a binary eutectic.

With three metals that are mutually insoluble in the solid state, the changes that occur in the composition of the liquid can be traced through

Fig. 12.

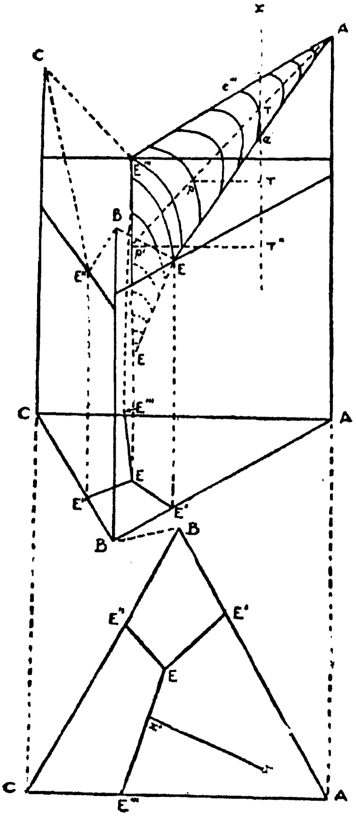


Fig. 13.

Fig. 14.

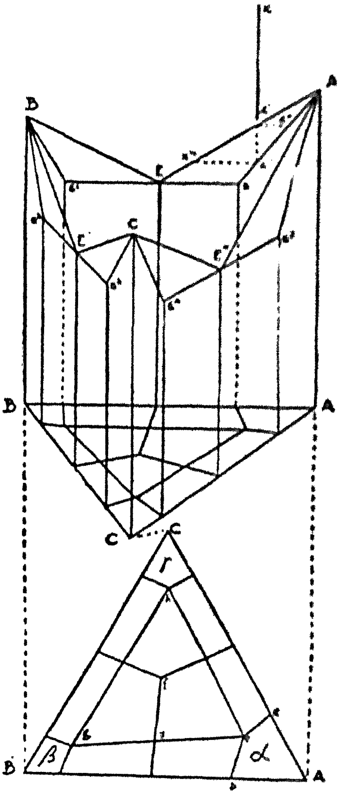


Fig. 15.

the whole period of solidification. Consider an alloy corresponding with the point *x*, figs. 12 and 13. On cooling, this mixture will begin to solidify when it reaches the point T, fig. 12—*i.e.*, the temperature of the isothermal line *e'''*, *e'*. The solid which then separates from the liquid consists of crystals of the pure metal A. This process of solidification proceeds with falling temperature, and the mother liquor becomes progressively impoverished in the metal A. Since, however, during this stage, there is only one metal separating the relative amounts of the other two metals, B and C in the mother liquor remain unchanged, and its percentage composition alters from the point x along the line x, x', fig. 13—*i.e.*, along a line drawn from the corner A through the point x, to meet the binary eutectic line E E‴. The actual composition of the mother liquor existing at any period can be readily determined, by drawing a line parallel with the base of the model from the desired point on the vertical temperature ordinates, say T′ to meet the line drawn from the point A through the point T. The composition of the mother liquor from alloy x when at the temperature of T′ corresponds with the point p. When the temperature T″ is reached, the mother liquor then corresponds with the point p', fig. 12, or x' in fig. 13. At this juncture the pure metal A ceases to separate alone, but crystallises simultaneously with some of the pure metal C, in the form of a binary eutectic, and the composition of the mother liquor then changes along the line x' E, fig. 13. During this period the composition of the liquid at any temperature can be ascertained by projecting a line parallel to the base of the model from the required temperature ordinate to meet the line x' E. The point of intersection indicates the composition of the liquid existing at that temperature. Finally, the liquid reaches the composition of the ternary eutectic E, when it undergoes no further change of composition, and the temperature remains constant until the whole of the alloy has solidified: at this stage the three metals A, B, and C are deposited at the same time.

In the case of ternary systems in which the metals are partially soluble in each other in the solid state, the conditions are much more complex than those just considered, and it becomes more difficult, if not impossible, to determine *a priori* the changes which occur during the solidification period; for not only does the concentration of the liquid alter, but the composition of the solid phase or phases may be changing at the same time.

In fig. 14 is shown a projection of a ternary system in which the metals are partially soluble in the solid state; the constitution of the system when just solid is indicated in fig. 15. The liquidi of the three binary systems are represented by the lines A E B, B E′ C, and C E″ A, and their respective solidi by the lines A S E S_1 B, B S_2 E_1 S_3 C, and C S_4 E″ S_5 A. An alloy X of the binary system A + B on cooling to the temperature x' begins to freeze with the separation of crystals of a solid solution x''. With further cooling the composition of the liquid alters along the line x' x''', and at the same time the composition of the solid crystals changes along the line x'' x'''' as a result of the fall in temperature and the changes which occur in the liquid phase. When the temperature of the line x''' x'''' is reached the whole of the alloy is just solid and the composition of the last trace of liquid corresponds with the point x'''. The difficulty of tracing quantitatively the changes which occur during the solidification period of ternary alloys that give rise to solid solutions is due to the fact that the actual and relative percentages of all three elements are varying both in the solid and liquid phases. If we take alloy x, fig. 15, as an example, this alloy begins to freeze with the separation of a solid solution of the metals B and C in A, which will be represented by a point somewhere on an isothermal line of the solidus running from the line A b to A e, the temperature represented by the isothermal line being the same as the initial freezing point of the alloy. The liquid ultimately corresponds in composition to a point on the line $d\,f$ whe the two phases α and β separate from the liquid and the composition of th liquid finally reaches that of the ternary eutectic *f*. It is only when th liquid corresponds with the composition of the ternary eutectic that th concentration of the solid phases can be determined *a priori*. At this stag the solids in equilibrium with the liquids are α, β, and γ, and their compositions are *c*, *g*, and *h* respectively.

CHAPTER II.

STRUCTURE OF METALS.

Structural Components: Crystals.—Having discussed the thermal changes which occur when alloys are cooled from temperatures at which they are quite liquid, down to atmospheric temperatures, the reader will be better able to understand their internal structural constitution, so far as it can be determined by examination under the microscope.

All metals and metallic alloys are composed of crystals which have grown either from metallic liquids or been deposited by electrical means from liquids of quite a different nature.

The first to take up this branch of metallurgical science was Dr. Henry Clifton Sorby, of Sheffield, who was also the founder of the study of the crystalline structure of rocks. The work of Martens in Germany, of Roberts-Austen, Stead, and Arnold in England, of Howe and Sauveur in America, and, in particular, of Osmond in France, has had a great influence upon the technique of this important and interesting subject.

Sorby regarded metals as being similar to igneous rocks. It is, however, impossible to examine metallic specimens in the same way as mineralogical sections—namely, with the aid of transmitted light. The method devised by Sorby, and now universally used, with only slight modifications for special purposes, is as follows:—A roughly prepared flat surface is given the specimens by filing, the file marks removed by rubbing upon coarse emery cloth, the process of obliterating the scratches continued by successively using finer and finer grades of emery cloth and paper. Finally, the last scratches made by the finest grade of paper are removed by polishing upon a wet pad of thick cloth or chamois leather, with the addition of some such powder as jewellers' rouge as an abrasive. It is advantageous to rub the specimens on each paper in such a manner that the scratches produced are approximately at right angles to those made in the previous operation. If the polishing be properly conducted the surface will be free from the finest of scratches, and in most cases will be quite mirror-like, and reveal no structure when examined under the microscope. It has been shown by Beilby that the absence of structure, on a perfectly polished metallic specimen, is due to a thin amorphous layer or film upon the specimen which is produced in the process of polishing. In order to render the structure visible, it is necessary to etch the surface by applying a suitable chemical reagent, which dissolves the amorphous film and attacks a given constituent more readily than another. If only one constituent is present some of the crystals become electro-positive to others, and are consequently attacked at a quicker rate. By this selective etching the structure of the metal is developed, and can be examined under the microscope.

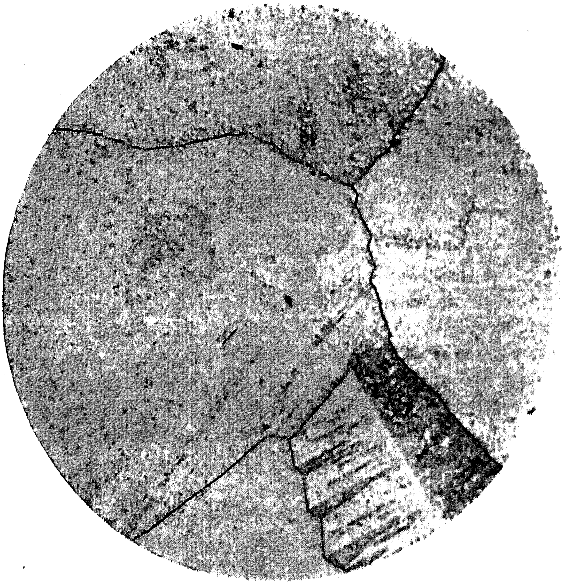


Fig. 16.— × 150.

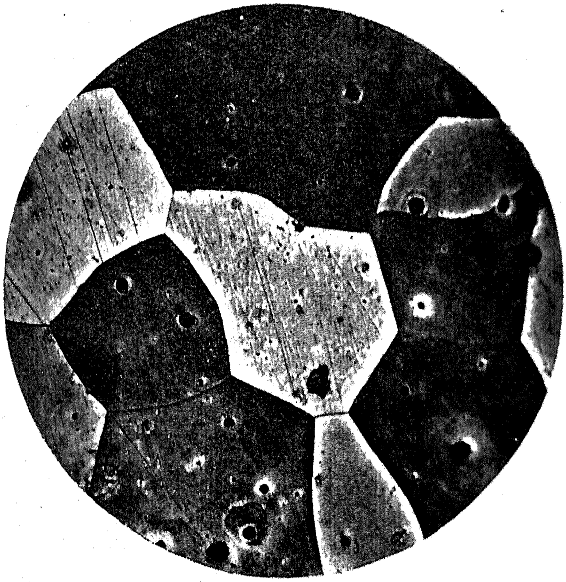


Fig. 17.—Structures Typical of Pure Metals (*Edwards* and *Andrew*) × 150.

Fig. 16 shows the typical microstructure of a pure metal after being prepared in the manner just described. The differential etching which very frequently occurs between crystals of the same composition is illustrated in fig. 17. In both cases it will be noticed that the boundaries of the crystals do not conform to any definite crystallographic shape. This is not because the units, or, as they are sometimes called, "crystal bricks," of which the crystals are composed, are irregular in shape, but merely because the conditions under which the structure was built up were such that the primary units could not arrange themselves in perfect sequence. With metals, it is only under exceptional circumstances that the crystal boundaries show a well-defined crystalline shape. This is due to the fact that the primary neuclei, upon which the various crystals have grown, take up different angles relative to each other. As the crystals are growing from their respective centres, at the same time and from the same liquid, they ultimately intercept each other's growth. In such cases it, therefore, follows that the outer shape of the crystal is defined by the space which is left by those surrounding it. Such crystals are called allotrimorphic crystals.

Dr. Rosenhain and Mr. Ewen[1] consider that the metal at the crystal boundaries is in a different state to that contained in the body of the crystals. They say :—A series of interstices are formed which are "smaller than the crystal units or bricks." The liquid residue left in these interstices will then be unable to crystallise, for the simple reason that there will be no space for the aggregation of the "liquid molecules" to form a "crystal molecule," and thus these portions must remain in the amorphous state. They also suggest that it is owing to the presence of this amorphous envelope that the crystal boundaries in etched specimens appear dark, on account of that phase being acted upon more readily by chemical reagents than the same metal in the crystalline state.

It has been previously mentioned that metals and alloys which are really composed of crystals of exactly the same chemical composition frequently appear to contain crystals of different colour (see fig. 17). This appearance does not indicate a difference of constitution, but is merely due to the crystals or their respective units possessing different orientations, and, therefore, reflecting the light, which falls upon them, at different angles. This can be readily proved by using oblique illumination and rotating the specimen through an angle of 180°. As the specimen is rotated the angle at which the rays of light fall upon the various crystal facets is changed, and crystals that were initially dark become light and *vice versâ*. Osmond has very aptly described this effect as resembling that resulting from the revolving light of a lighthouse.

Crystal Twinning.—A very characteristic appearance, which is frequently seen in metallic crystals, and is known as "twinning," is also caused by a difference in the orientation of two or more adjacent crystals of the same chemical composition and constitution. Twin crystals possess a boundary on one side which is common to both, and runs across their whole length or breadth. As these boundaries are usually perfectly straight, or consist of a series of straight lines, when viewed under the microscope, they give the impression that they have been formed by the breaking up of a parent crystal

---

[1] "Intercrystalline Cohesion in Metals," *Journ. of Inst. of Metals*, No. 2, 1912

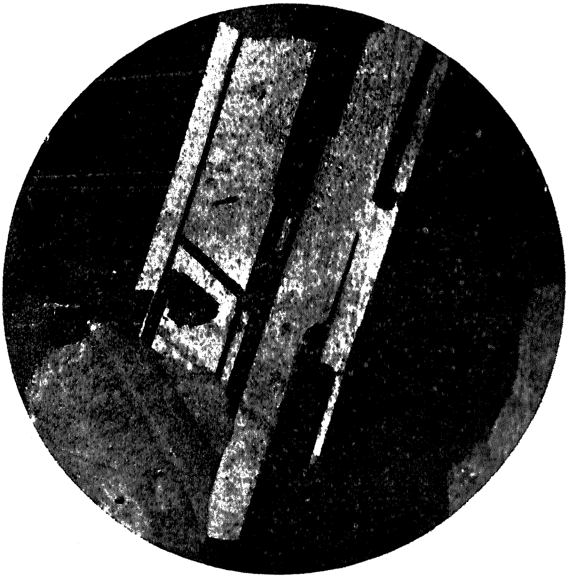


Fig. 18.— × 150.

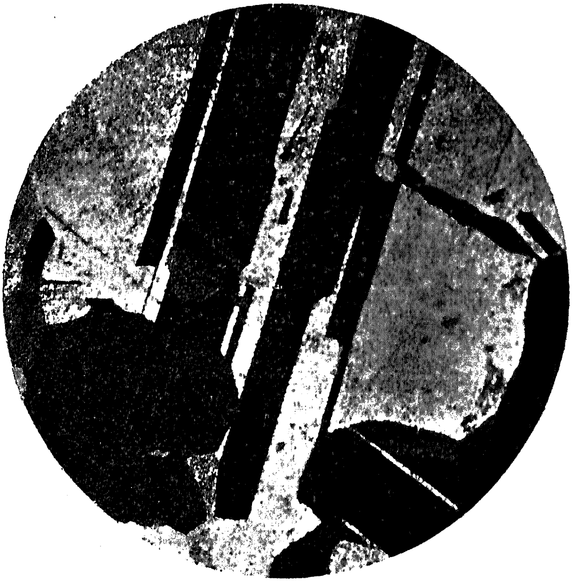


Fig. 19.—Twin Crystals Viewed under Oblique Light at Different Angles, in this instance differing by about 180° (*Edwards* and *Carpenter*). × 150.

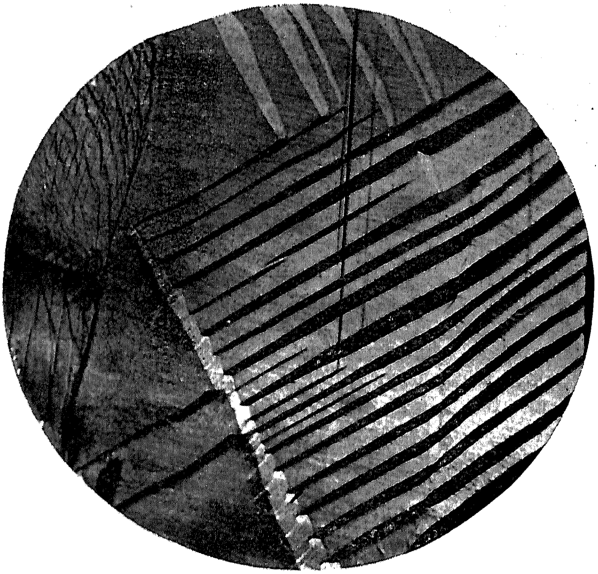


Fig. 20.—Twin Crystals Produced by Direct Mechanical Straining of Tin. × 150.

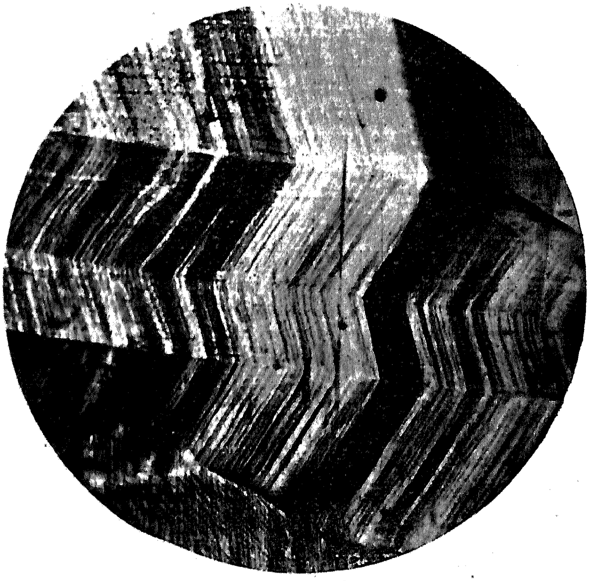


Fig. 21.—Showing Slip-bands passing through Twin Crystals (*Edwards* and *Carpenter*). × 150.

In some instances this is unquestionably what has occurred, but in others it is not, strictly speaking, what has happened. Sir Alfred Ewing[1] says:—"Twinning is sometimes the direct result of straining actions, but is more often produced when a metal, after having been strained, is annealed. The nature of twinning is, perhaps, most easily intelligible if the crystals are considered as built up of brickbats, and that after one layer had been completed the next layer has all the bricks turned round through an angle of 180°. The result would be a twin formation. In the microscope, twinning is shown by the appearance of a dark band in a crystal parallel to the lighter portion or *vice versâ*. Under strain twinning is indicated by an abrupt change in the direction of the slip bands."

Twin crystals that have been formed as a result of straining followed by annealing are shown in fig. 18, and the fact that this appearance is entirely due to the orientation of the crystals is definitely indicated in fig. 19, which represents the same area as seen in fig. 18, after rotating the specimen about 180°. There seems to be no clear idea of the mechanism by which twin crystals are developed on annealing metals which have been previously strained. Whether they are formed by the growth on annealing of exceedingly fine twin crystals, which are formed during the mechanical deformation, or not, it is at present impossible to decide. This is a feasible explanation, and is in perfect accord with what little we know of the subject, but as yet it can only be regarded as tentative. Be that as it may, it is now known that the crystals of certain metals are capable of being twinned as a result of direct mechanical strains, and that the width of these twins varies from the excessively fine up to comparatively very broad bands. Twin crystals, which have been produced by straining, are illustrated in fig. 20.

Slip-bands.—This term was first introduced by Messrs. Ewing and Rosenhain,[2] and is applied to the appearance which they observed upon polished surfaces of metals that had been subjected to slight but permanent deformation. Fig. 21 serves the double purpose of showing slip bands, and the marked change in their direction as they pass from one twin crystal to another. The above workers have explained the formation of these slip bands in the following manner:—During deformation the metal undergoes a process of slipping or gliding upon the crystallographic planes, which gives rise to a series of steps on the polished surface, and when viewed under the microscope these minute steps are seen as parallel lines running across the crystals.

The structure of an alloy containing two constituents is shown in fig. 22. In this case the white constituent has been deposited from the solid solution and squeezed to the boundaries of the original crystals. The dark areas still contain an excess of the white constituent, which has been prevented from separating by rapidly quenching in water. With slow cooling this excess is readily deposited, and is seen in fig. 23.

The structure of an eutectic alloy is shown in fig. 24, where the dark globular areas represent primary crystallites and the background the real eutectic portion.

---

[1] "The Inner Structure of Metals," *Journ. of Inst. of Metals*, 1913, No. 2.
[2] *Philosophical Transactions*, 1900, vol. cxciii., p. 352.

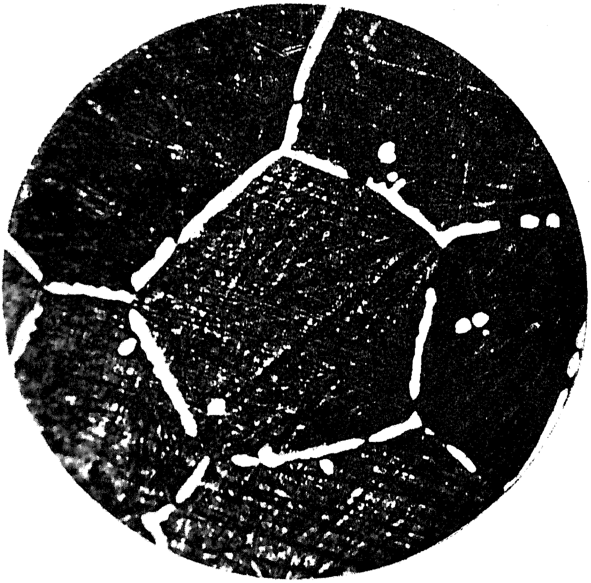


Fig. 22.— × 150.

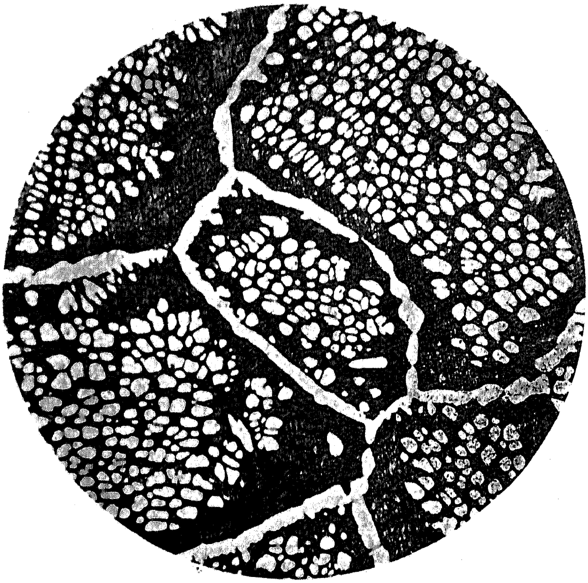


Fig. 23.— × 150.

Showing Change of Structure at Different Temperatures (*Edwards* and *Andrew.*)

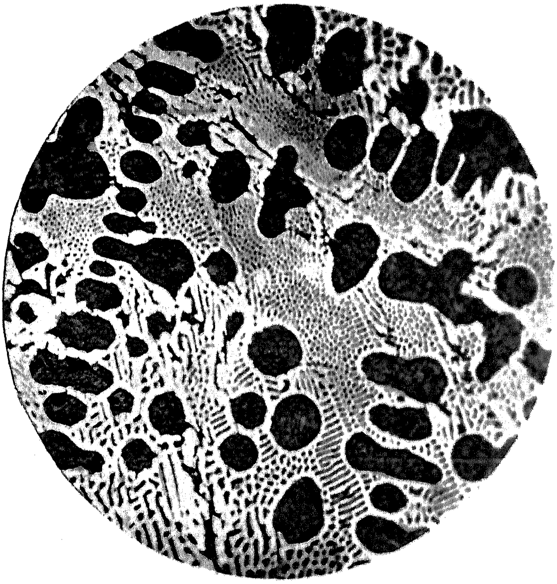


Fig. 24.—Eutectic Structure with Slight Excess of one Constituent. × 150.

CHAPTER III.

IRON.

So far as can now be ascertained, the first intimation that there is any discontinuity in the properties of iron or steel with a variation of temperature was made by Gilbert in 1600. He discovered that when a magnet is heated to redness it loses all traces of magnetism. No important scientific advance appears to have been made after Gilbert's discovery until 1868, when Tchernoff[1] first noticed the connection between the so-called critical point and the hardening of steel. In the year 1869 Dr. G. Gore[2] stated that "simply by heating a bar of iron to redness, a whole series of changes occur in its molecular structure, its magnetism, its dimensions, its cohesive power, its specific heat, its thermo-electric capacity, and its electric-conducting power." This was followed in 1873 by Professor W. F. Barrett's[3] discovery of the phenomenon known as "recalescence." He found that if a piece of steel, and especially a steel containing about 1 per cent. of carbon, be heated to red heat, and then allowed to cool, it progressively becomes darker until a certain temperature is reached, when there is a sudden evolution of heat, which is sufficient to raise the temperature of the mass, and render it perceptibly brighter.

The next addition to our knowledge of this subject came from F. Osmond[4] in 1887, and was a most noteworthy qualitative and quantitative advance. With the aid of the thermo-electric pyrometer devised by H. Le Chatelier, Osmond was the first to determine the thermal data for iron and iron-carbon

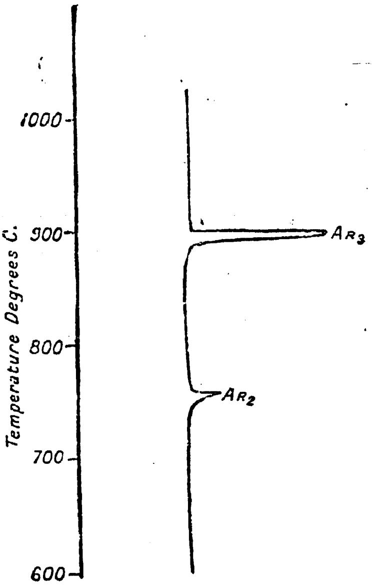


Fig. 25.

---

[1] Tchernoff, Paper communicated to the Imperial Russian Tech. Society, April and May, 1868.

[2] "On the Molecular Movements and Magnetic Changes in Iron at Different Temperatures," *Phil. Mag.*, 4th series, vol. xl., p. 177, Sept. 1870.

[3] "On Certain Molecular Changes occurring in Iron Wires at a Low Red Heat," *Phil. Mag.*, 4th series, vl. xlvi., p. 472, 1873.

[4] "Transformations du fer et du carbone dans les fer, les aciers et les fontes blanches," *Mémoires de l'artillerie de la marine*, vol. xxiv., p. 573, 1887; also "Critical Points of Iron and Steel," *Iron and Steel Inst.*, No 1, 1890.

alloys when heated and cooled. A derived differential cooling curve of pure iron is shown in fig. 25. It will be observed that on cooling iron there is an abrupt arrest in the cooling at 900° C., which is caused by the evolution of a considerable amount of heat in the specimen.

Immediately after this thermal disturbance there is a marked acceleration in the rate of cooling. A second retardation in the fall of temperature then becomes evident at 760° C. A third point occurs at 700° C., with the introduction of carbon to iron, and this point increases in magnitude as the percentage of carbon is raised to about 0·90. Following Tschernoff, Osmond applied the letter A to the critical point associated with the hardening of steels. Since, however, he found more than the one critical point, and discovered that they had different physical meanings, it was necessary to distinguish between them, and he introduced the terms A_1, A_2, and A_3, A_3 being applied to the change which occurs at the highest temperature—namely, 900° C.—A_2 for the arrest at 760° C., and A_1 for the point due to carbon at 700° C. It frequently happens that the temperatures at which these critical points are observed are not exactly the same when the specimens are heated as when they are cooled, and on that account it was necessary to introduce a further distinction in order to denote whether any particular thermal change under discussion occurred during heating or cooling.

In order to meet this need Osmond introduced the letters *c* for heating (chauffage) and *r* for cooling (refroidissement). Thus the expression Ar_3 is used to denote the evolution of heat at 900° C. when pure iron is cooled, and Ac_3 for the absorption of heat, which corresponds to the reverse change when the metal is heated.

It is fairly obvious that these thermal changes, which occur in almost chemically pure iron, must be brought about by some internal crystalline or molecular transformation inside the mass, and whilst it is universally considered that the change which occurs on cooling at 900° C. is due to an actual allotropic transformation in the iron itself, there has been and still is some uncertainty in regard to the physical interpretation of the Ar_2 point. In view of this, it is of some importance carefully to note the interpretation which Osmond gave in his pioneer work. He said :—" Since the point Ar_3 is the more individualised the nearer the iron approaches to purity, it is evident that this point corresponds with a molecular modification of iron. Iron is a polymorphous element like sulphur, silicon, etc. In the present state of our knowledge, it is difficult to say whether Ar_2 is a second distinct molecular modification of Ar_3, or whether it is simply the end of Ar_3 retarded by the presence of a little carbon. . . . It is merely probable that Ar_2 is the retarded end of Ar_3. I, therefore, accept this view provisionally, and until it is disproved, and shall assert that iron below Ar_2 possesses the molecular form α, and assumes above Ar_3 the allotropic form β. Between Ar_3 and Ar_2, when these two points are distinct, the metal is a mixture of the two variations α and β."

In discussing the theoretical cause of hardening steels by quenching, Osmond made the statement that "β-iron is hard and brittle by itself at the ordinary temperature, and that α-iron is soft." A cooling curve of electrolytic iron published by Roberts-Austen[1] shows, in addition to the

---

[1] Fifth Report to Alloys Research Committee, *Proc. Inst. of Mech. Engs.*, 1899, p. 35.

Ar_3 and Ar_2, two evolutions of heat which occur at about 487° C. and 261° C. These two points were observed after the specimen had been heated *in vacuo* to 1,300° C. three successive times; but after repeated heatings of the metal *in vacuo* they become so small that it is impossible to identify them with certainty. Hence there is little doubt that they are due to the presence of hydrogen occluded in the iron. Roberts-Austen also found that the presence of hydrogen increased the magnitude of the Ar_3 and Ar_2 points; but this increase could be eliminated by repeated heatings *in vacuo*.

Professor Arnold[1] found that the recalescence of Ar_3 occurs much more sharply and between narrower limits of temperature when hydrogen and other occluded gases are removed. In no case, however, has it been found possible to eliminate, by heating for very prolonged periods *in vacuo*, the points Ar_3 and Ar_2 of the purest iron yet experimented with. Judging from the experimental evidence he obtained from iron containing 0·04 per cent. of carbon, Professor Arnold[2] concluded that the point Ar_2 was not in any way connected with the point Ar_3. Arnold considered that Ar_2 was a physical point due to the passage of hot iron from a plastic to a crystalline condition.

In the discussion on this paper Osmond stated that he himself found that Ar_2, and, not as he originally supposed Ar_3, corresponds to the loss of magnetism which occurs when iron is heated, which supports the view that there is a decided difference between Ar_3 and Ar_2. In consequence of this individual existence of Ar_3 and Ar_2 Osmond concluded that there are three distinct allotropic varieties of iron—viz., α, β, and γ. The ranges of temperature in which these varieties exist are—α-iron from 0° to 760° C.; β-iron from 760° to 900° C.; and γ-iron from 900° to 1,505° C.

In recent years there has been a tendency to revert to Osmond's original, or a somewhat modified interpretation of the Ar_2 point, and regard it as the lower limit of the Ar_3 change. An excellent summary and criticism of the data bearing on this question has been published by Benedicks,[3] and the subject is further discussed in papers read by Stead and Carpenter,[4] and by Sauveur,[5] before the Iron and Steel Institute.

Benedicks suggests that the Ar_2 point is due to the α-iron holding a certain limited amount of γ-iron in solution. According to this view, iron at temperatures between 900° and 760° C. consists of a solid solution of molecules of γ-iron in crystallised α-iron, which possesses different properties from its constituents. This idea certainly seems theoretically possible, and should be carefully taken into consideration. It is, however, necessary to remember that it is only a suggestion, for Benedicks himself says:—"The possibility of A_2 corresponding to an actual discontinuity can certainly not be denied. . . ." With the view of testing this theory, Carpenter carefully determined the heating and cooling curves of exceedingly pure electrolytic iron containing 99·967 per cent. of iron and only 0·008 per cent. of carbon.

---

[1] Discussion, Second Report Alloys Research Committee, *Inst. of Mech. Engs.*, 1893, p. 102.

[2] "The Physical Influence of Elements on Iron," *Iron and Steel Inst. Journ.*, 1894, No. 1, p. 110.

[3] *Journ. of Iron and Steel Inst.*, 1912, No. 2, p. 242; 1914, No. 1, p. 407.

[4] Carpenter, *Journ. of Iron and Steel Inst.*, 1913, No. 1, p. 315; 1913, No. 2, p. 119.

[5] *Journ. of Iron and Steel Inst.*, 1913, No. 2, p. 171.

Typical curves taken after repeated heating and cooling *in vacuo* are shown in fig. 26. It will be noticed that on cooling there is only a slight indication of a point beginning at about 760° C. and reaching a maximum at 743° C., whilst on heating there is no evidence of the corresponding change. At this stage it should be noted that thermal transformations are seldom so well defined on heating as on cooling curves. The accumulated evidence certainly indicates that the Ar_2 point decreases in magnitude as the purity of the iron is raised, but at present it would be unwise to assert that Ar_2 would be entirely absent in chemically pure iron.

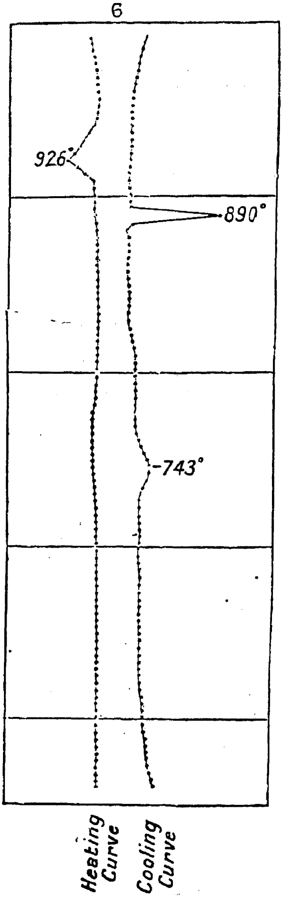


Fig. 26.—(*Carpenter*).

As regards Benedick's suggestion, perhaps the most decisive test to apply would be to cool the purest iron to below the Ar_2 point, then heat it to a temperature below 900° C. (Ac_3), and again cool. If Benedicks' theory be correct, the Ar_2 ought not to appear after this treatment, because all the γ-iron molecules should be thrown out of solution with the first cooling, and it would seem impossible for them to redissolve at temperatures below 900° C. This experiment has not yet been made.

Whatever the true solution of this highly theoretical problem may be, the fact remains that in ordinary iron there are two thermal changes on cooling—one at 900° C. and the other at 760° C. Whether the 760° C. point is or is not a true allotropic transformation is a matter of little importance. In any case it possesses all the characteristics of, and practically may therefore be regarded as, an allotropic change.

When at temperatures within the three ranges, 0° to 760°, 760° to 900°, and 900° to 1,505° C.—that is, when in the α, β, and γ condition—the properties of iron are remarkably different. Thus, α-iron is magnetic, it will not dissolve carbon, and the crystals do not seem capable of twinning; β-iron is non-magnetic, it will dissolve little or no carbon, and will not form twin crystals; γ-iron is non-magnetic, it will readily dissolve carbon, and will form twin crystals.

Magnetic Properties.

Curie's [1] determinations of the magnetic intensity of iron with varying temperature show a well-defined change (fig. 27) at a temperature of about

---

[1] "Properties magnetiques des corps," *Annales de Chimie et de Physique*, 1895, serie 4, vol. v, p. 289.

760°, which corresponds with A_2, and a second break at (900° C.) the Ar_3 point. Weiss and Foëx[1] have also confirmed these results, but by plotting the inverse magnetic intensity $\frac{1}{x}$ against temperatures they obtained a diagram (fig. 28) wherein the discontinuities are brought more into prominence.

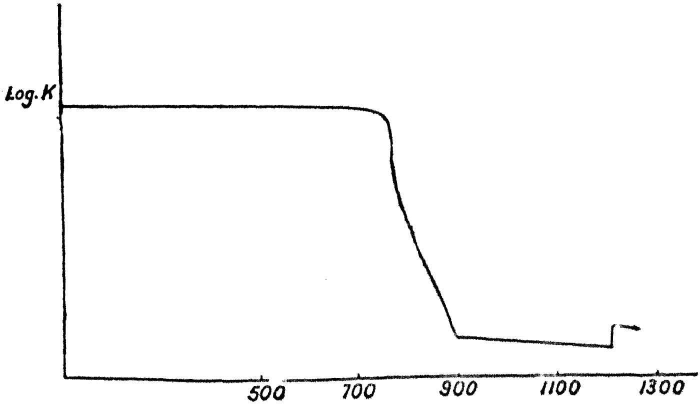


Fig. 27.

Dr. K. Morris[2] has determined the magnetic permeability and hysteresis of pure iron at temperatures up to about 1,050° C. Fig. 29 is one of the curves from Dr. Morris' paper. From this curve it will be seen that there is a slight rise in the permeability as the temperature reaches about 150° C.; this is followed by a fall at 200° C. Another marked increase then becomes evident, and reaches a maximum between 400° and 500° C. There is a most remark-

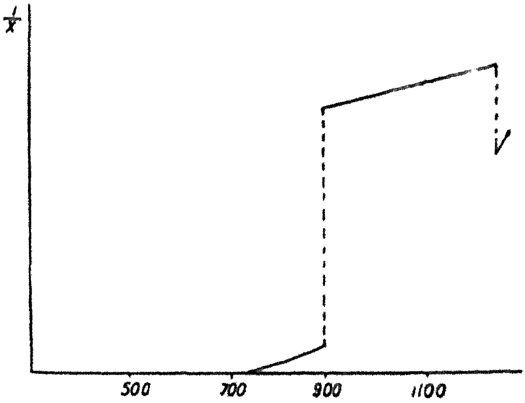


Fig. 28.

---

[1] *Archives des Sciences*, Genève, 1911, serie 4, vol. xxxi., p. 89.

[2] *Phil. Mag.*, Sept. 1897.

able change beginning at 570° C., the permeability rapidly increasing with the temperature until 760° C. is reached, after which it suddenly drops to zero. This change corresponds with the $\alpha \rightleftharpoons \beta$ inversion. It is interesting to note that the magnetic permeability is by no means negligible at about 900° C.

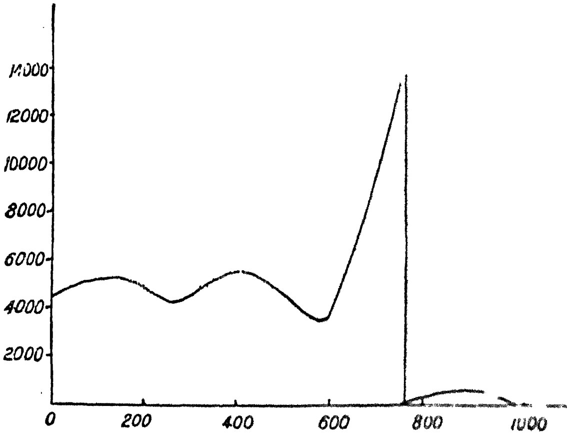


Fig. 29.

Dilatation.

The curves showing the variations in the volume of iron with rising

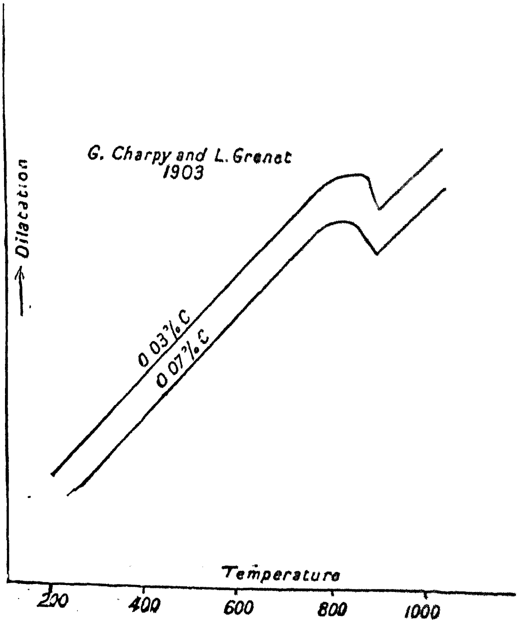


Fig. 30.

temperature, as drawn from Charpy and Grenet's[1] experiments, are shown in fig. 30. These two curves, obtained from irons containing 0·07 and 0·03 per cent. of carbon, clearly show that even such small differences in carbon content exert a very decided influence upon this property at temperatures approximating to that of the A_2 change. Thus, as the temperature rises to about 760° C., the expansions in both cases are quite continuous. From that temperature upwards the character of the two curves is different, but at 900° C. (which corresponds to the A_3 point) the sudden contraction which occurs is practically the same in each case.

Electrical Resistance.

The variations in the electric resistance in iron, with rising temperature, has been determined by Boudard,[2] who found that there are marked changes in this property at 770° C. and at 890° C.

Specific Heats of Iron.

The specific heats of iron, as determined by Dr. Harker, are shown in Table I. From these figures it will be seen that there is a marked change at 900° C. There are other discontinuities at lower temperatures, but they are too irregular for them to be associated with any definite physical transformation.

TABLE I.—MEAN SPECIFIC HEAT BETWEEN 0° and T°.—S_0^T.

T.	S_0^T.	T.	S_0^T.	T.	S_0^T.
200	·1175	550	·1361	850	·1647
250	·1204	600	·1396	900	·1644
300	·1233	650	·1440	950	·1612
350	·1257	700	·1487	1,000	·1557
400	·1282	750	·1537	1,050	·1512
450	·1311	800	·1597	1,100	·1534
500	·1338				

Structure of Iron.

The microstructure of pure iron, when it is in a normal condition at the ordinary temperature is shown in fig. 31 at a magnification of 200 diameters. In this instance the etching of the polished surface was made by immersing the specimen in a 1 per cent. solution of nitric acid in alcohol for about half a minute. Under these conditions only the general outlines or boundaries of the crystalline aggregates of the mass are rendered visible under the microscope, which are seen in the photograph as polygonal grains. This network does not give any definite indication of the true crystalline character of the metal itself, or, in other words, of the numerous crystalline units of which those grains are composed, because under the usual conditions which prevail in the manufacture of iron, the crystal units have not sufficient time and freedom to arrange themselves in such a manner that the crystalline aggregate shows true crystal faces. The true crystalline habit of iron has formed the subject of many researches, and the problem has been attacked in a number of ways.

---

[1] *Bulletin de la Société d'Encouragement*, 1903, vol. civ., pp. 464-882.

[2] *Iron and Steel Inst.*, 1903, No. 1, p. 299.

Dr. Percy states that Wohler[1] obtained cubic crystals from cast iron plates which had been exposed to a white heat for a long time, and also octahedral crystals from the cavities of a large unsound cast iron roll.

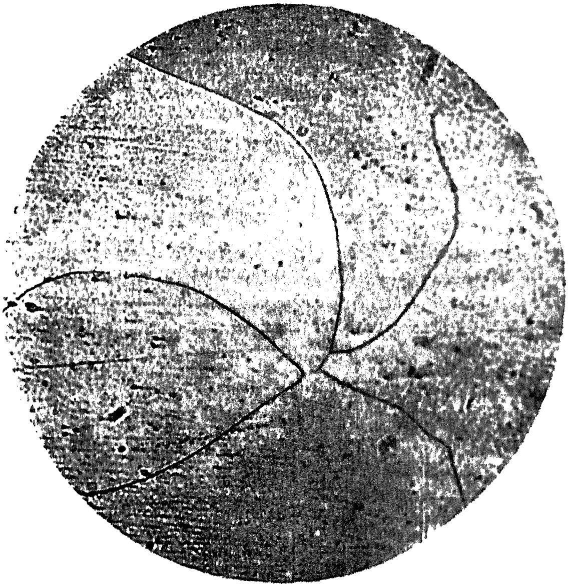


Fig. 31.—Structure of Pure Electrolytic Iron (*Stead* and *Carpenter*).

Dr. Percy[2] also refers to a flat bar of iron which had been allowed to remain for a long time in a pot of molten glass, in which he found the cleavage planes arranged perpendicular to the external surface. The surface of this bar was covered with fine hexagonal markings. He also states that Prof. Miller, of Cambridge, found Bessemer iron to consist of an aggregation of small cubes.

Fuchs[3] was of the opinion that wrought iron crystallised in the cubic system.

Working on the micro-crystalline structure of large masses of very pure wrought iron which had been very slowly cooled from a white heat, T. Andrews[4] observed that the linear dimensions of what he described as the primary crystals would average about 0·01 inch, but he also observed that

[1] John Percy, *Iron and Steel*, 1864, p. 3.
[2] *Ibid.*, p. 3.
[3] *Ibid.*, p. 4.
[4] *Proc. Roy. Soc.*, vol. lviii., pp. 59-64.

these were built up of units of much smaller size. He made measurements of the angles of the facets of these units, or, as they are frequently called, molecular crystals, and found that in most cases the angle readings were about 120°, which suggests that the crystalline structure or form of the metal is hexagonal. He also observed perfectly formed cubical crystals.

A very substantial advance to our knowledge in this direction was made by the publication in 1898 of a paper by J. E. Stead.[1] In this paper it is conclusively shown that when iron is in a stable condition at temperatures below 760° C.—*i.e.*, in the α form—it crystallises in the cubic system. One of the photographs which Stead then published is shown in fig. 32, where the cubical form of the crystalline units can be very clearly seen. In the same paper, moreover, many facts of great value, regarding the effect of thermal treatment upon the structure and properties of pure iron, were also brought to light, which also have a direct bearing upon the allotropic conditions in which iron is capable of existing at high temperatures. He found that, "in pure wrought iron and low carbon steel having fine crystal grains, produced either by forging or certain heat treatment, the grains increase in size slowly at 500° C., and more rapidly as the temperature is raised to about 750° C., and it is possible by heating at about 700° C. for a few hours to develop granular masses of exceeding coarseness." He also pointed out that when pure iron which had been made coarsely crystalline in this way was heated between 750° and 870° C. the structure was not altered to an appreciable extent, but as soon as the temperature of about 900° C. was passed, the coarse crystals were again broken up into small ones (see fig. 33). Further heating to 1,200° C. did not produce any apparent difference in the dimensions of the crystals.

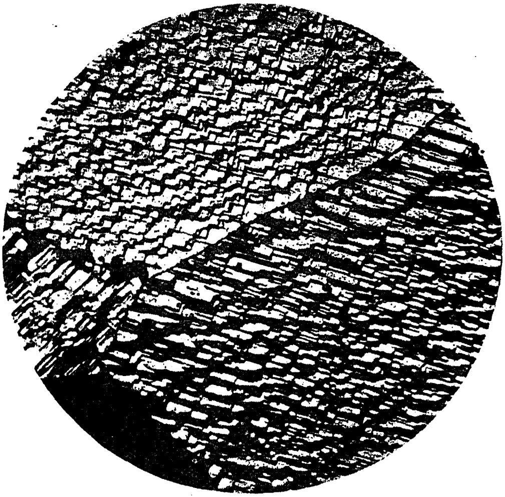


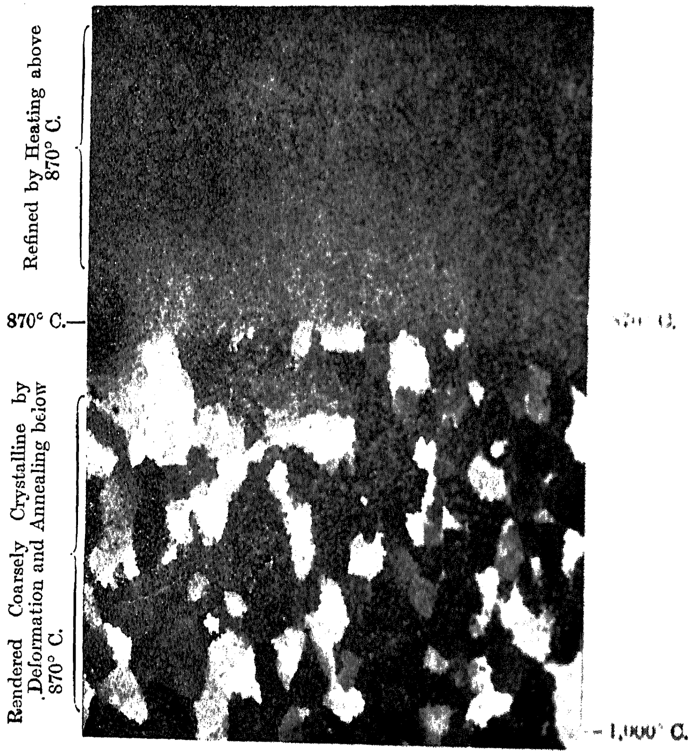
Fig. 32.—Crystalline Character of the Interior of Large Crystals revealed by Deep Etching (*Stead*).

---

[1] *Iron and Steel Inst.*, 1898, No. 1, p. 145.

These facts are very interesting, because they leave no room to doubt that on passing through the A_3 point at 900° C. iron undergoes a decided change in its crystalline condition. Thus, when very coarse grains of β iron are heated from just below 900° C. to a temperature just above 900° C. they are transformed in γ-iron, and this change is accompanied by a recrystallisation of the whole mass, which gives rise to much smaller crystals.

Dr. Stead and Professor Carpenter[1] have found that the behaviour of thin strips of very pure electrolytic iron differs in many ways from that of ordinary wrought iron or mild steel. Thus, the crystals of cold worked electrolytic iron do not become coarsened by annealing between 700 and 800° C. in the same way as mild steel. The heat treatment, which refines the coarsely crystalline structure of mild steels,—namely, heating to just above 900° C.—actually brings about excessively rapid crystal growth in electrolytic iron. This particular effect only seems to be obtained when the thickness of the iron sheet or strip does not exceed a certain critical figure, which is between 0·011 and 0·012 of an inch. In the case of electro


Refined by Heating above 870° C.
870° C.—
870° C.
Rendered Coarsely Crystalline by Deformation and Annealing below 870° C.
—1,000° C.

Natural Size.
Fig. 33.—(*Stead*).

---

[1] *Iron and Steel Inst.*, 1913, No. II, p. 119.

lytic iron the crystal growth occurs after the material has cooled below the Ar_3 change, and takes place so quickly that only three seconds are required for it to be completed. It can be entirely prevented by quenching the strips from temperatures above the Ar_3 point.

Fig. 34 is an extremely interesting example of crystal growth. It represents the structure of electrolytic iron, in which the outer edges of the specimen were heated to above the Ac_3 point, but the central portion did not reach that change before the sheet was again cooled. Hence the crystals in the centre have remained practically unaltered, whilst those in the outer parts have grown to a remarkable size.

In neither of the publications just referred to were the investigators able to detect any change in the crystalline structure of iron at temperatures corresponding with the A_2 thermal transformation.

By etching specimens of iron in fused calcium chloride at different temperatures, Saniter[1] endeavoured to determine the crystalline changes as the metal passes through the A_3 and A_2 points. The results he obtained were quite interesting and instructive. When etched in this way at temperatures above the A_3 point the metal gave unmistakable signs of crystal twinning, and the boundary lines of these twins seem to indicate that iron when in the γ condition is in the form of rhomboid crystals. At lower temperatures no twinning was observed, and no change could be detected as the metal passed the A_2 point. Osmond and Cartaud[2] have paid considerable attention to this subject, and arrived at the following conclusion :—" The only positive conclusion that we can draw from these researches is that the three allotropic varieties of iron, although they all crystallised in the cubic system, present well-defined specific characters, and cannot have the same internal structure."

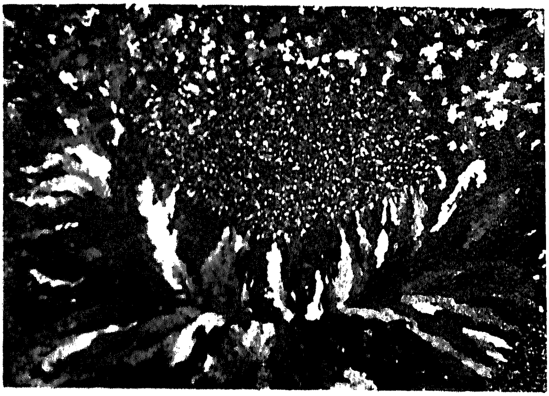


Fig. 34.—Showing Coarse Crystallisation in Electrolytic Iron by Heating above Ac_3 Change (*Stead* and *Carpenter*).

It is known that there are three varieties of the cubic system : the simple cube, which only has intersections at its summits; the centred cube, which has another intersection at its centre; and the cube with centred faces, with an intersection at the centre at each of its faces. It is, therefore, possible that the three varieties of iron correspond to these three systems, but, in view of the very remarkable changes that occur on passing through the A$_3$ point, it would seem that at that temperature there is a much more radical change in the crystalline nature of the element.

---

[1] *Journ. Iron and Steel Inst.*, 1897, No 2.

[2] *Ibid.*, 1906, vol. iii.

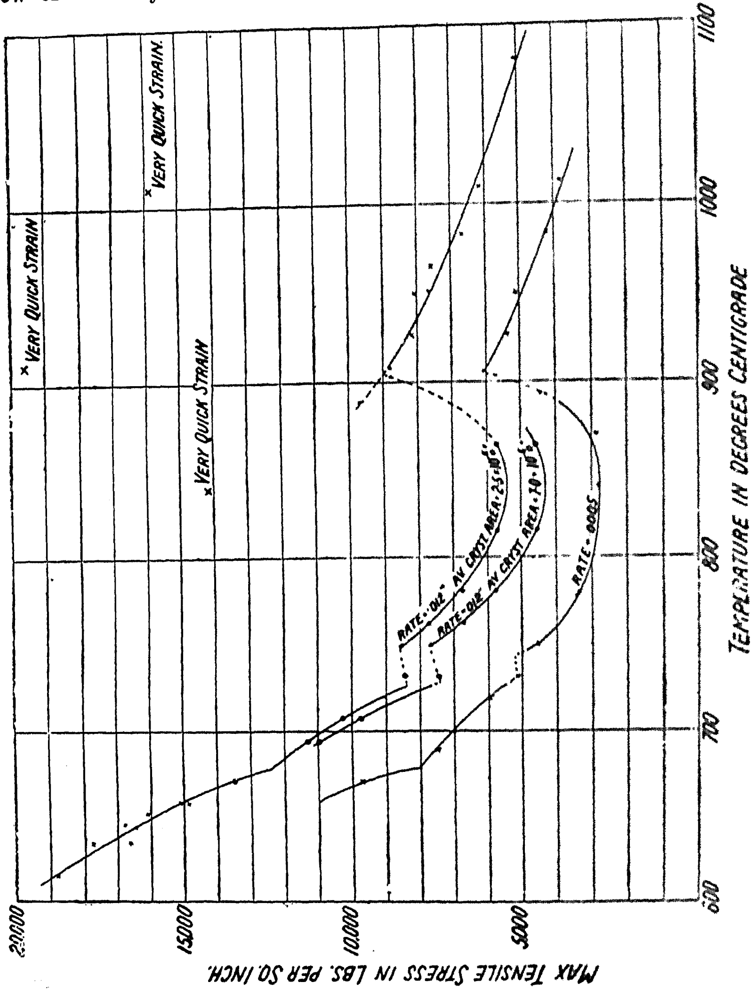


Fig. 35.

Working on the structure of iron at high temperatures, Rosenhain and Humprey[1] obtained evidence which indicates that between 0° and 1,000° C. iron can exist in three distinct modifications which possess widely different mechanical properties. Although the temperatures were not exactly determined, they considered that the changes were coincident with the points A_3 and A_2. These authors were also the first to demonstrate that iron at high temperatures—in the γ state—undergoes deformation on straining by a process of slip on the cleavage or gliding planes, which may or may not be accompanied by mechanical twinning.

---

[1] *Proc. Roy. Soc.*, A, vol. lxxxiii., 1909.

In a later publication the same investigators[1] have made very careful determinations of the tenacity of mild steel at temperatures up to 1,000° C. The results they obtained are graphically illustrated in fig. 35, where the tenacity in pounds per square inch are plotted against temperatures. It will be observed that there is a marked change in the mechanical properties of the metal at 900° C. A similar but much less decisive break occurs at about 750° C. The composition of the material experimented upon was as follows:—

Carbon, ...	0·106 per cent.
Manganese, ...	0·395 ,,
Silicon, ...	trace
Phosphorus, ...	0·050 ,,
Sulphur, ...	0·075 ,,

Perhaps the most remarkable fact which was brought to light in this work was that iron when at a temperature just above 900° C. has a higher tensile strength than it has when at a temperature between 730° and 900° C. Therefore, it seems quite safe to conclude that γ-iron is a hard variety of the metal. The change of direction shown on the curves between 850° and 900° C. is difficult to understand, unless it is due to the gradual increase in the amount of solid solution present as the temperature is raised.

---

[1] *Iron and Steel Inst.*, 1913, No. 1.

CHAPTER IV.

THE CONSTITUTION OF THE IRON-CARBON SYSTEM—EQUILIBRIUM DIAGRAMS.

In a previous chapter attention has been drawn to the fact that the temperature at which an element passes from the liquid to the solid state, and also that at which it changes from one allotropic modification into another, are materially influenced by the presence of foreign elements it may hold in solution. The effect of carbon upon iron is strongly marked; for example, the temperature at which pure liquid iron solidifies is 1,505° C.[1] whereas when iron contains about 4·0 per cent. of carbon in solution the mixture remains perfectly liquid down to 1,130° C.

Much smaller quantities of carbon exert a remarkable influence upon the temperatures at which the thermal critical points A_3 and A_2 occur. As these changes are accompanied by certain more or less well defined alterations in the properties of the pure metal, and also of its alloy, it is quite evident that the action of the carbon is twofold. First, by combining with the iron, it imparts certain properties to the alloy characteristic of the compound which is formed; and, secondly, it delays or lowers the temperature at which the normal transformations take place. Both these factors make it necessary to modify the practical treatment of the resulting steel, according to its particular composition. In other words, the best temperatures for casting, annealing, and forging, etc., depend upon the composition of the steel. The first requirements in the scientific study of carbon steels are a thorough knowledge of the chemical compounds and constituents that iron and carbon are capable of forming, the ranges of temperature and composition in which those constituents are capable of existing for an indefinite period, the conditions which bring about their dissociation, and the means by which they can be retained at temperatures outside their stable region. The importance of a complete understanding of these considerations, so far as they are now known, in regard to iron-carbon alloys, is by no means confined to carbon steels, but extends to what are called special steels—*i.e.*, those containing other elements which have been intentionally added. All these considerations are either embodied in, or may be deduced from, the equilibrium diagram, which may, therefore, be justly regarded as a most important chart in regard to the metallurgy of steel.

Karsten[2] (1824) was probably the first to observe that when annealed steels were dissolved in dilute hydrochloric or sulphuric acids a carboniferous compound was always left as a residue. Similar observations were made by Caron[1] and by Rinman,[2] and the latter gave to this residue the name "cement carbon." Sir F. Abel[3] confirmed Karsten's observations, and by acting upon the drillings with a solution of potassium bichromate and sulphuric acid, found that the residues contained 6·7 per cent. of carbon and 93·3 per cent. of iron. These percentages correspond with the formula Fe_3C. He obtained as much as 96 per cent. of the total carbon contained in the steel as a carbide residue. Müller[4] and Ledebur[5] also found the same results by using very dilute sulphuric acid. The acid was allowed to act upon the steel at atmospheric temperatures for several days, a current of hydrogen or coal gas being maintained to prevent contact with the air. By treating the carbide with hot acid it is decomposed with the evolution of hydrocarbons. Arnold and Read[6] obtained results which confirmed Abel's work. They employed an electrolytic method, and obtained the carbide almost chemically pure in the form of plates. Osmond and Werth[7] also isolated the carbide, Fe_3C, and found that if the steel be dissolved in cold nitric acid (1·8 to 1·20 specific gravity), there remains in the first instance a brown flocculent residue which contains 44·59 per cent. of carbon, 8·05 per cent. of iron. 22·5 of water, and 24·86 per cent. of oxygen and nitrogen. This readily dissolves when the liquid is heated, and imparts a brown colour to the solution, which forms the basis of the Eggerts colour test for carbon.

---

[1] H. C. H. Carpenter, *Journ. Iron and Steel Inst.*, No. 3, p. 290, 1908.

[2] *Archiv für Berglau und Hüttenwesen*, vol. viii., p. 3.

Although the molecular formula of the carbide of iron is generally regarded Fe_3C, it is not known with certainty. It might, for instance, be Fe_6C_2 or Fe_9C_3. Sir Robert Hadfield has recently offered a substantial prize for the elucidation of the problem, and with the object of stimulating research in this direction.

The next advance was made by F. Osmond,[8] who, in his original paper dealing with the Ar_3 and Ar_2 critical points of pure iron, gives a detailed account of the effect of carbon upon those points, and shows that the presence of even small quantities of carbon gives rise to an entirely new critical point at 710° C., which he described as the Ar_1, or carbide change. He found that in proportion to the increase in the amount of carbon present, Ar_3 is rapidly lowered and first joins Ar_2, then what may be called the double point Ar_3 and Ar_2 descends in turn, and finally coincides with the Ar_1 point in the presence of about 0·9 per cent. of carbon. Hence in the case of steels containing 0·9 per cent. of carbon only one, rather large, evolution of heat occurs —viz., the Ar_1, or, as it is sometimes called, the $Ar_{3,\,2,\,1}$ point.

Sir W. Roberts-Austen made many researches, and was the first to attempt systematically to determine[9] and graphically represent the whole of the thermal transformations through which the iron-carbon alloys pass,

---

[1] *Comptes Rendus de l'Academie des Sciences*, vol. i., vi., p. 43.
[2] Erdmann's *Journ. für Praktische Chemie*, vol. c., p. 32.
[3] *Engineering*, vol. xxxix., pp. 150 and 200.
[4] *Stahl und Eisen*, 1888, p. 291.
[5] *Ibid.*, 1888, p. 42.
[6] *Journ. Chem. Soc.*, vol. lxv., p. 788.
[7] *Annales des Mines*, Series 8, vol. viii., p. 5.
[8] *Journ. Iron and Steel Inst.*, 1890, No. 1, p. 38.
[9] *Proc. Inst. Mech. Engs.*, 1899, p. 35.

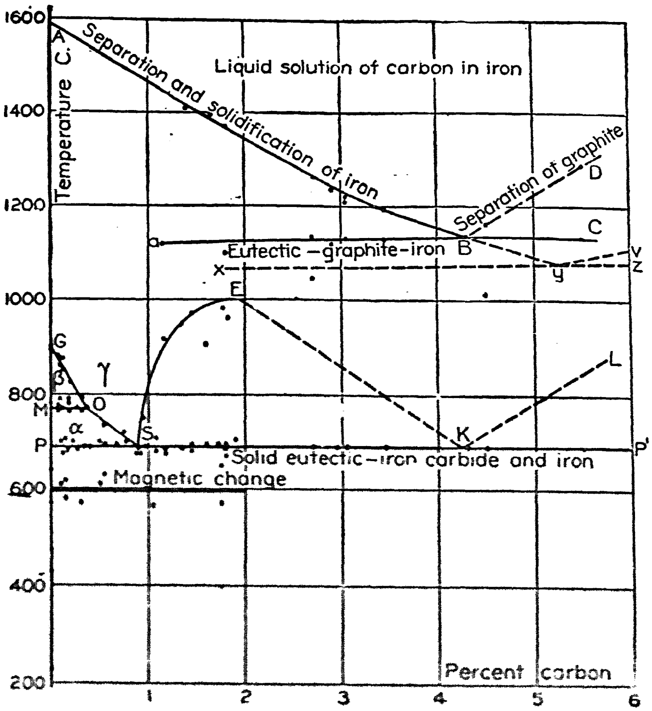

1600
1400
1200
1000
800
600
400
200
Temperature C.
A
Separation and solidification of iron
Liquid solution of carbon in iron
Separation of graphite
D
C
B
a
Eutectic —graphite-iron
V
Z
X
y
E
G
β
γ
M
O
α
S.
P
K
L
P'
Solid eutectic—iron carbide and iron
Magnetic change
Percent carbon
1
2
3
4
5
6

Fig. 36.

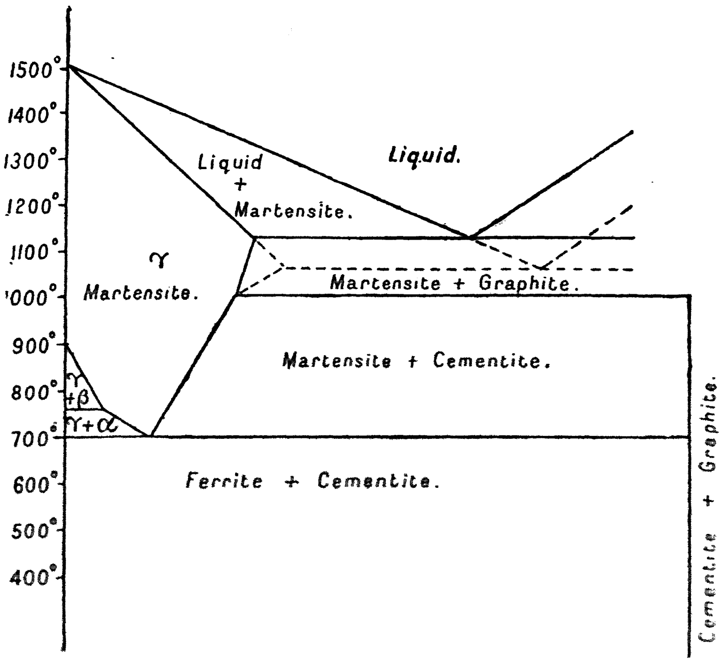

1500°
1400°
1300°
1200°
1100°
1000°
900°
800°
700°
600°
500°
400°
Liquid.
Liquid + Martensite.
γ Martensite.
Martensite + Graphite.
Martensite + Cementite.
γ +β
γ+α
Ferrite + Cementite.
Cementite + Graphite.

Fig. 37.

on cooling from temperatures at which they are quite liquid down to about 200° C. (fig. 36). It was from Osmond and Roberts-Austen's data that Roozeboom[1] constructed an equilibrium diagram to develop the theoretical constitution of the iron-carbon series. This diagram, which is shown in fig. 37, was admittedly tentative, and later on Professor Carpenter and Mr. Keeling[2] made very careful determinations of the thermal changes (see curves, figs. 39 and 40). In addition to confirming the main changes found by Roberts-Austen, and making certain corrections in regard to temperatures, they found two other thermal changes which had not been noticed by previous investigators. They did not, however, construct another diagram as a result of their work, but simply introduced their observed points on Roozeboom's diagram (fig. 38).

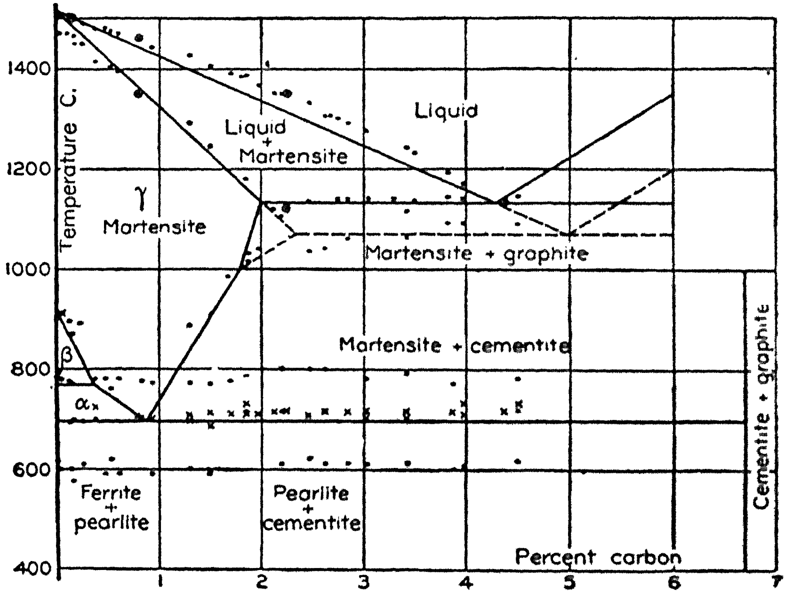


Fig. 38.

Gutowsky has determined the solidus line for mixtures containing less than about 2·0 per cent. of carbon, by quenching small sections from various temperatures and subsequently examining them under the microscope. In this way the presence of any liquid which may exist at the temperature from which the alloy was quenched can be detected in the specimen as circular white areas inside the crystals or as white envelopes around them (see fig. 41). The part which was liquid at the high temperature etches differently in the quenched specimen, because it contains more carbon than the part which was solid, and the quenching prevents the carbon being again distributed by diffusion. The solidus, as determined in this way, is shown in fig. 42.

---

[1] *Journ. Iron and Steel Inst.*, 1900, No. 2, p. 311

[2] *Ibid.*, 1904, No. 1, p. 224.

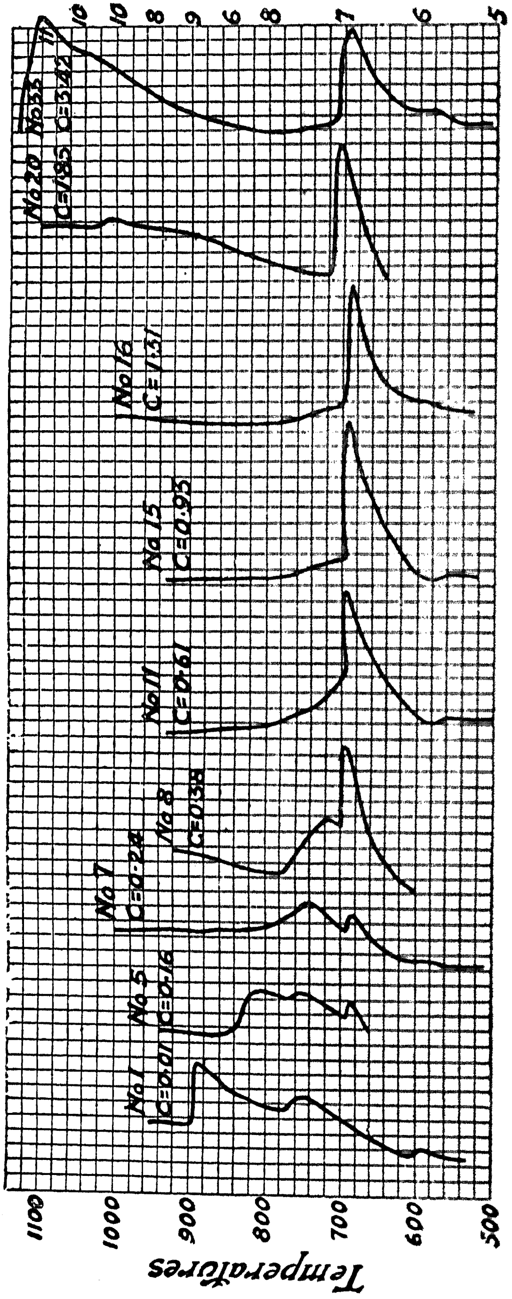


Fig. 39.—(Carpenter and Keeling)

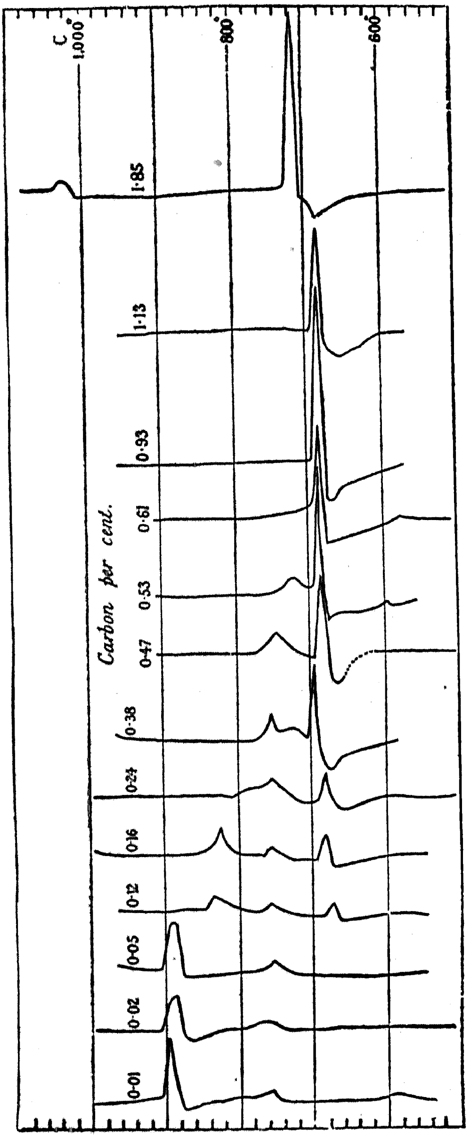


Fig. 40.—Replotted from Carpenter and Keeling's Data (*Rosenhain*).

In 1908 Upton [1] published a modified equilibrium diagram, which includes

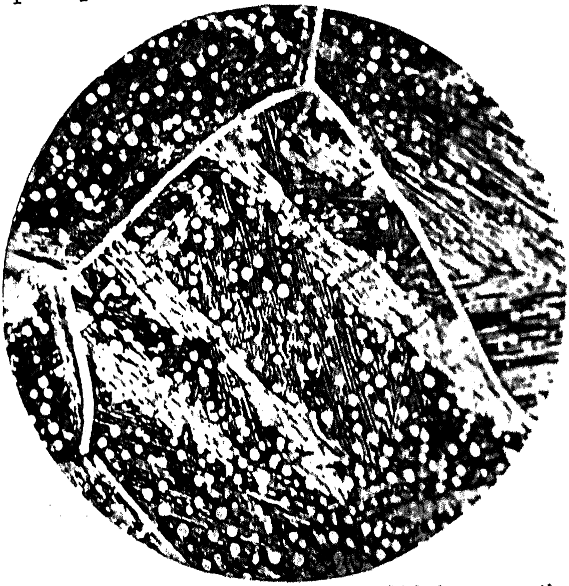


Fig. 41.—Alloy Quenched from Temperature at which it was partly Liquid White Boundaries and Circles represent Parts that were Liquid.

the two critical changes found by Carpenter and Keeling He considers

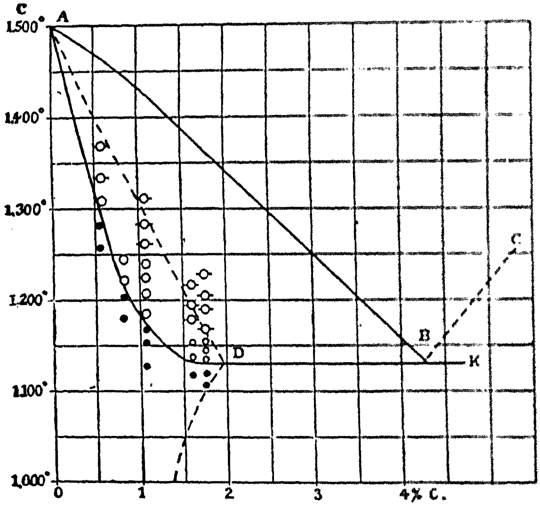


Fig. 42.

that these two changes correspond with transformations in the chemical constitution of the iron carbide. A totally different type of diagram, which is known as the stable, or iron and graphitic carbon diagram representing the true equilibrium conditions of these alloys as they are understood by Benedicks, Ruer, Le Chatelier, Charpy, and others, has also been published. It will readily be seen that it is not a simple matter to give a clear description of the constitution of this series, because there are still many details which require careful investigation. When considering steels alone, however, this difficulty is not so great, because many of the controversial questions may be left out of consideration. Broadly speaking, there is no fundamental difference of opinion as regards the changes which occur when steels are heated or cooled under normal conditions. Hence, in the general discussion

---

[1] *Amer. Journ. Phys. Chem.*, vol. xii., No. 7, 1908.

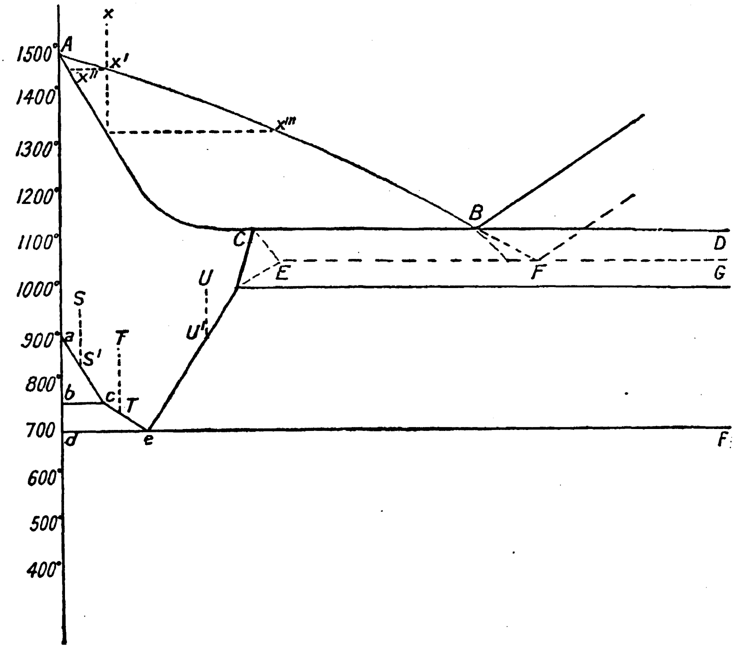


Fig. 43.

of the solidification and subsequent cooling of steel, it makes no real difference which of the modern diagrams are taken. At a later stage, however, it will be necessary to consider in some detail the prevailing ideas relating to the conditions upon which there is some uncertainty, but which may have a possible bearing upon the subject under examination.

Taking Roozeboom's diagram with Gutowsky's modified solidus (fig. 43) as representing the constitution of the iron-carbon system, the changes which steels undergo on cooling are as follows :—

The vertical ordinates represent temperatures, and the horizontal ordinates correspond with the percentages of carbon and iron contained in the alloys. The slightly convex liquidus curve A B indicates the temperatures above which any particular alloy of known carbon content is perfectly liquid, and also the temperature at which it will deposit its first crop of crystals as the mass cools. These solidifying or freezing temperatures can be readily ascertained by projecting a vertical line from a point on the horizontal ordinates which corresponds with the desired percentage of carbon, and noting the temperature indicated by the point at which that line intersects the liquidus curve. The liquidus curve clearly indicates how the freezing temperature is influenced by the amount of carbon present—*e.g.*, there is a continuous fall from 1,505° C. for pure iron to 1,130° C. for a mixture containing about 4·3 per cent. of carbon.

The solidus lines A C B D represent the temperatures below which the various mixtures are perfectly solid. It will be noticed that the solidus for the series containing less than 2·0 per cent. of carbon—that is, those steels which fall to the left of the point C—is a sloping line, whilst for those steels containing more carbon it is horizontal. This is because the crystals that are deposited from the liquid in the former are constantly changing in composition during the period of solidification, but in the latter, whatever the initial composition of the alloy may be when the temperature of the line C B D is reached, the composition of the liquid always corresponds with the eutectic alloy which solidifies at a constant temperature without any further change in composition.

Alloys containing less than 2·0 per cent. of carbon when quite solid consist of a series of homogeneous solid solutions which are of the same constitutional character. They contain all the carbon as carbide of iron held in solution by the iron which is in the γ condition. At lower temperatures this group may conveniently be subdivided into three further classes, which pass through somewhat different changes as they cool to temperatures just below the line *d e f*, 700° C. They are (*a*) those containing less than 0·45 per cent. of carbon, (*b*) from 0·45 to 0·90 per cent. of carbon, and (*c*) from 0·90 to 2·0 per cent. of carbon.

The effect of carbon upon the Ar_3 and Ar_2 critical points of pure iron is clearly illustrated in the series of cooling curves shown in figs. 39 and 40, and the points or ranges seen on those curves are represented by the lines *a c* and *c e* in the diagram, fig. 43. From the curves it will be seen that even small quantities of carbon have a marked lowering effect upon the temperature of the Ar_3 change, and with about 0·45 per cent. of carbon Ar_3 becomes practically coincident with the Ar_2 change. As the carbon is still further increased the double change $Ar_3 + Ar_2$ is progressively lowered, until, with 0·9 per cent. of carbon, only the Ar_1 or carbide change is evident.

As is clearly shown on the cooling curve of a steel containing only 0·12 per cent. of carbon, the Ar_1 change appears almost with the first introduction of carbon to iron. The precise meaning of the various lines in the iron-carbon diagram will no doubt be more readily understood by giving a detailed description of the changes through which certain typical steels pass as they cool from the liquid state down to ordinary atmospheric temperatures.

The carbon content of a steel represented by the point x, fig. 43, is 0·5 per cent. At the temperature x it is perfectly liquid, and remains in that condition as it cools until the temperature x', 1,475° C., is reached. At this stage the mass begins to solidify by the deposition of a number of solid crystals. The composition of the crystals that are formed at this period is represented by the point x''; they contain 0·10 per cent. of carbon, or 0·40 per cent. less than the liquid from which they were formed. In consequence of this selective separation of relatively pure crystals the remaining liquid becomes correspondingly enriched in carbon, and as the freezing temperature of steel is lower the higher the carbon content, it follows that this secondary liquid must possess a lower freezing temperature than the initial mixture. Therefore, before it is possible for any more crystals to be formed from the liquid the temperature of the mass must be lowered. With this necessary fall in temperature a second crop of crystals is formed and deposited upon those first produced. As the chemical composition of the crystals deposited is governed by the actual composition of the mother liquid, the second batch of crystals contains a slightly higher percentage of carbon than those formed in the first instance. With ideal theoretical conditions – that is, if sufficient time were allowed during the solidification period – the slight difference in the percentage of carbon contained in each successive layer of crystals would be neutralised by the process of diffusion.

In the ordinary freezing of an ingot of steel the conditions are not such as to permit of complete diffusion, and it is, therefore, practically impossible to get the theoretical progressive change in the composition of the solid and liquid during the solidification period. If the rate of cooling could be kept slow enough to allow of perfect equilibrium being established, the last trace of liquid to be converted into solid from the steel, x, fig. 43, would have the composition x'''. In proportion as the cooling is quicker than is theoretically demanded, the composition of the liquid will be thrown more and more to the right of x. The compositions of the crystals and the liquid that are in equilibrium with each other at any temperature can be determined by drawing a horizontal line at the desired temperature to meet the solidus and liquidus curves, the points of intersection representing the composition of the liquid and solid phases.

Turning now to the changes which occur in carbon steels as they cool from temperatures at which they are just solid down to just below 700° C., it will perhaps be well to describe in detail the cooling of one member of the three groups already mentioned.

It has been previously stated that the addition of carbon to iron lowers the Ar_3 change, and when 0·45 per cent. of carbon is present it is coincident with, or, to be more correct, commences at the same temperature as the Ar_2 point in pure iron. This is the first natural subdivision of the carbon steels, and comprises a series which undergo the same physical changes as they cool. On cooling a steel containing – *e.g.*, 0·20 per cent. of carbon (s, fig. 43) from temperatures just below the solidus line – it remains constitutionally the same until it reaches the point s' (fig. 43) (840° C.), when it begins to deposit a certain amount of β-iron from solution; and since this form of iron will not hold carbon or carbide of iron in solution, or at all events only a very limited amount of that element, the remaining γ solution from which the β-iron separated is relatively enriched in carbon. As a further result, the temperature at which it is possible for more β-iron to separate from the secondary γ solution is lowered, and it is necessary for the temperature to fall a little before the amount of β-iron can increase. This kind of change, in the carbon percentage of the γ solution and growth of β-iron, proceeds as the temperature falls, and is exactly similar to the separation of a pure salt from an aqueous solution, or that of a pure metal from a liquid alloy. It will, therefore, be seen that the presence of carbon modifies the ordinary γ-iron into β-iron change of pure iron, which is theoretically completed at one temperature, by making the change extend over a range of temperature. When the temperature of the steel is 760° C., corresponding to the line *b c*, all the possible β-iron has been formed, and the remaining γ solution contains 0·45 per cent. of carbon, represented by the point *c*. As β-iron will not dissolve carbon, it follows that the β iron which is formed when these steels are cooled below the line *b c* will be precisely the same as if it had been produced from pure iron as it passes through the Ar_3 change. It will have the same properties and change into α iron at the same temperature—viz., 760° C. That being the case, when these steels are at the temperature of the line *b c*, there are three phases or constituents existing together—namely, pure β and α-iron, and the solid solution represented by the point *c*. Under these conditions there is no degree of freedom, so the three phases can coexist in equilibrium only at that particular temperature. Therefore, the β-iron is bodily transformed into α-iron, and as the temperature falls still further α-iron is directly deposited from the solid solution without the intermediate formation of β-iron.

When this state of affairs has been reached the subsequent transformations for the steels of the first group are exactly the same as those which will be considered for the second. A steel containing 0·60 per cent. of carbon may be taken as a typical example of this group. This steel (T, fig. 43) undergoes no constitutional change after it has solidified until the temperature has fallen to T′, 740° C., at which a certain amount of α iron is formed. The separation of this α-iron, which holds little or no carbide of iron in solution, necessarily increases the percentage of carbon left in the remaining solid solution, whence it follows that the temperature must again fall before any more α-iron can be formed. With further cooling the quantity of α iron present increases, and the carbon content of the solid solution is progressively raised until at 700° C. the composition of the latter corresponds with 0·90 per cent. of carbon—that is, with the eutectoid point *e* (fig. 7). It is, therefore, obvious that in all cases steels containing up to 0·90 per cent. of carbon, when at a temperature just above that of the line *d e*, consist of α iron and the solid solution containing 0·9 per cent. of carbon. The relative amount of those two constituents is governed by the actual carbon content of the steel.

All carbon steels show the Ar_1 thermal critical point which corresponds with the breaking up of the eutectoid solid solution into α-iron and carbide of iron. The temperature of this change is usually about 700° C. The magnitude or intensity of the Ar_1 change is governed by the amount of eutectoid solution which is being decomposed. It is hardly necessary to say that in a steel containing 0·9 per cent. of carbon this reaches a maximum, when the whole of the steel passes through the Ar_1 transformation. With steels containing from 0·9 to 2·0 per cent. of carbon the changes again differ somewhat from those previously considered. As an example of this group we may take a steel containing 1·5 per cent. of carbon. As this alloy (U, fig. 43) cools a certain amount of carbide of iron is deposited at the temperature *u′*, 900° C., and as the cooling proceeds the quantity of carbide increases, and the carbon left in the solid solution decreases until at the temperature of the line *d e f* the carbon contained in the latter is shown by the eutectoid point *e*. As in the instances previously considered the eutectoid solution is then decomposed into α-iron and carbide of iron.

It will be noticed that the line *d e f*, which represents the carbide change, is drawn as a perfectly horizontal one. This indicates that the Ar_1 change occurs at the same temperature in all steels of varying carbon content. Actually, however, it has been clearly shown in the data published by Carpenter and Keeling that the temperature of this change, as observed by taking cooling curves, gradually rises as the carbon increases above 0·9 per cent., and in the presence of about 2·0 per cent. of carbon it takes place at about 20° C. higher than in a steel of the eutectoid composition. The reasons for drawing this line horizontally are purely theoretical. From the phase rule we know that three phases can coexist in equilibrium, in a binary system, only at one temperature. At the Ar_1 point there are three phases—namely, α-iron, carbide of iron, and the solid solution of the eutectoid composition—hence, theoretically, this change should take place at the same temperature throughout the system. In all probability the differences observed in the cooling curves are due to supercooling in the case of those steels containing less than 1·0 per cent. of carbon. With steels containing higher percentages of carbon this supercooling is apparently prevented by the presence of the free carbide of iron, which forms before the temperature of the Ar_1 change point is reached.

There are many instances known where the presence of an excess of one constituent induces the inversion to occur at the theoretically correct temperature. Whilst, therefore, it is quite in order to illustrate the Ar_1 change by a horizontal line in the equilibrium diagram—which is a diagram representing the temperatures at which the inversions would occur, and the compositions which the phases taking part in those reactions would assume if sufficient time were allowed—it is necessary to remember that these ideal conditions are seldom attained in the ordinary course of cooling masses of steel.

We have now to consider certain facts which indicate that carbide of iron is an unstable constituent, and will, under certain conditions, decompose into iron and graphitic or free carbon. It has long been known that iron containing about 4·0 per cent. of carbon, if cooled very quickly from the liquid state by casting in a chill mould, will contain the whole of the carbon as carbide of iron, but when cooled slowly practically all the carbon occurs in the graphitic state. Further, the carbide of iron contained in a quickly cooled iron can be decomposed by heating the mass to a temperature of about 1,000° C. Hence there is no doubt that iron carbide has only a limited range of stability. Even in steels graphitic carbon can be produced quite readily when the carbon content is above 0·90, but with lower percentages this change is brought about only by prolonged annealing just below 700° C. From these facts it is clear that, in order to illustrate the conditions of perfect equilibrium it is necessary to introduce some modification of the diagram as described. In other words, whilst in that diagram are depicted the various changes which any given carbon steel will pass through on being heated and cooled at the rates which prevail in most steel-manufacturing conditions, it does not take into account the decomposition of carbide of iron which occurs under more favourable circumstances. Fig. 43 is, therefore, generally referred to as the metastable equilibrium diagram of the iron-carbon system.

With perfect equilibrium it is considered by many that iron carbide does not exist in the free state, and, therefore, that constituent has no position in the true equilibrium diagram. The "perfectly stable" condition of the iron-carbon alloys, as understood by Heyn, Ruer, Benedicks, and others, is represented in figs. 44, 45, and 46. It will be noticed that in each of these diagrams graphitic carbon is depicted as one of the constituents which should be deposited from the liquid eutectic B if the mixture be cooling sufficiently slowly at that temperature, while if the cooling be quick the mass becomes supercooled when an artificial eutectic F is produced, from which carbide of iron, and not graphitic carbon, separates from the liquid as one constituent. There is no doubt that this view is in accordance with the facts

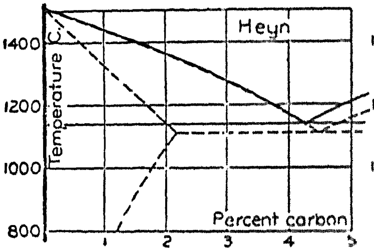


Fig. 44.

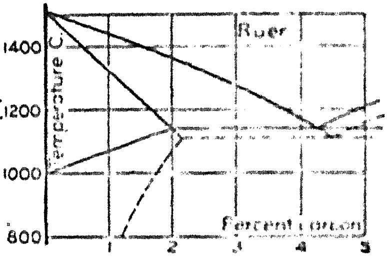


Fig. 45.

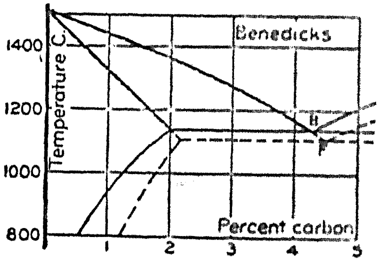


Fig. 46.

so far as they are known. Within the solid solution range (viz., those mixtures containing less than about 2·0 per cent. of carbon) there is every reason for saying that Benedicks' diagram (fig. 46) more closely corresponds with the known experimental facts than figs. 44 and 45. Thus, for example, pure iron, when embedded in carbon and heated to 900° C., will readily take up carbon which definitely indicates that stable solid solutions of the two can exist at that temperature. This fact is not indicated in figs. 44 and 45.

Yet another diagram has been constructed by Upton (fig. 47), who sees no reason to believe that a stable and metastable condition of equilibrium exists in these alloys. Upton reviews the previous publications relating to this question, and concludes that there are three carbides of iron, viz., Fe_6C, Fe_3C, and Fe_2C. It is certainly quite possible that the carbide Fe_3C may not be the only compound which can exist in this series of alloys, but the evidence supporting the existence of Fe_6C and Fe_2C is very slender. In the first place, the inversion at 800° C., which Upton introduces in his diagram for mixtures containing more than about 1·0 per cent. of carbon, is based upon the pyrometric work of Carpenter and Keeling, and whilst those investigators observed a discontinuity in their cooling curves, a reference to figs. 39 and 40 will show how very slight it was. It is certainly not sufficient to conclude that it corresponds with a definite change in the constitution of the carbide of iron. Further, the whole of Upton's conclusions are apparently negatived by the fact, which has been demonstrated by Arnold, that almost all the carbon of a pure carbon steel containing 1·4 per cent. of carbon is in the free state after heating for 72 hours at 1,000° C. and then slowly cooling.

This fact conclusively shows that carbide of iron, Fe_3C, is unstable below 1,000° C., and possibly at somewhat higher temperatures. However, considering that carbide of iron has been repeatedly isolated, there can be no doubt that such a chemical compound exists, and it seems necessary to allocate a position for it in the true equilibrium diagram. In other words, there seems good reasons for supposing that carbide of iron must be capable of existing for an indefinite length of time over a limited range of temperature, otherwise it is difficult to understand how it could be formed at all. With the object of supporting this contention, the diagram (fig. 48) has been constructed, showing carbide of iron as one of the constituents to separate from the liquid eutectic, and to remain in a stable condition when at temperatures within the lines *a b*, *c d*, and *e f*. At the temperature, however, of the lower line it decomposes into graphitic carbon and the solid solution *c*. Considered in the light of this diagram, a white iron is formed by the quick cooling or

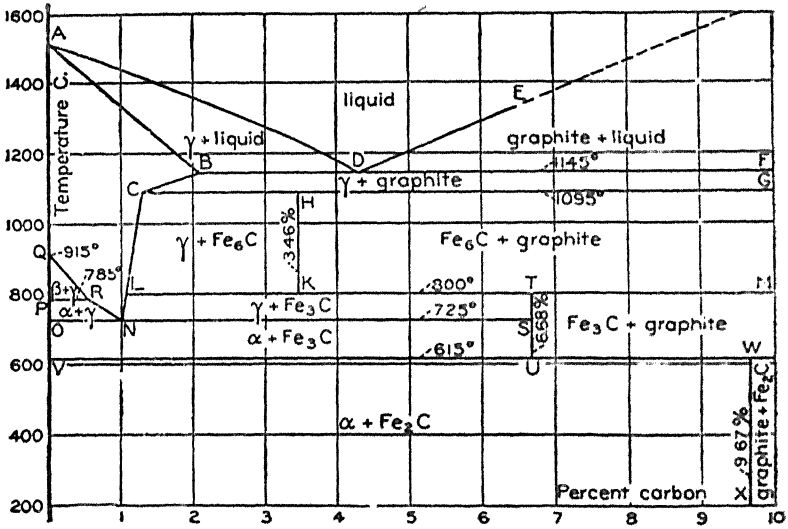


Fig. 47.

chilling, and not by the supercooling of the liquid eutectic, simply because insufficient time has been allowed for the carbide of iron first formed to decompose on passing through the temperature of the line *ef*. The metastable conditions are illustrated by means of the dotted lines.

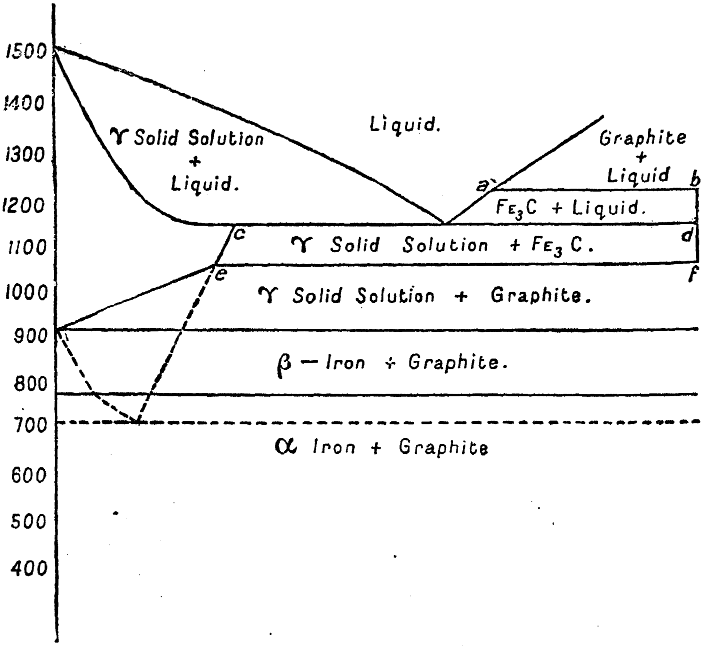


Fig. 48.

CHAPTER V.

MICROSTRUCTURE OF IRON-CARBON STEELS.

BEFORE turning to the detailed study of the structural constituents of the iron-carbon system, as they appear under the microscope, it will be advisable to give a brief description of the origin of the nomenclature that is used for the subject, and to draw attention to the utility of correlating that nomenclature with the experimental facts that are known and embodied in the equilibrium or constitution diagram. Sorby, who was the first investigator in this branch of metallurgical science, regarded steel essentially from a mineralogist's point of view, and he naturally applied a mineralogical terminology to the microscopical constituents that were discovered in steel. Hence, after selecting a name either in honour of some particular scientist, or from an analogous mineralogical constituent, the suffix " ite " was attached. The terms " austenite," " troostite," " sorbite," and " pearlite " have since been coined in this way.

As our knowledge of the real constitution of steels at all temperatures extended, and it became possible to construct a chart or diagram graphically illustrating the whole of the physical and chemical changes through which they pass as the temperature is varied, it became evident that there were more names in use than there could actually be found definite room for inside the chart. For that and other reasons many keen controversies have arisen as to the scientific accuracy or meaning of some of the terms that have been used in the metallography of steel. As will be seen, this state of affairs arose in no small degree because the microscopical analysis of steel was well advanced before the general, physical, and especially the thermal data were anything like complete, and also because the laws of physical chemistry were not seriously applied to the study of metallic alloys until a comparatively recent date. In the case of the non-ferrous alloys, the nomenclature of the structural constituents has been based almost entirely upon the physical data that are embodied in the equilibrium diagrams, which fact places the subject upon a firm scientific basis, and eliminates the little differences of opinion that are not of vital importance, but which are frequently the cause of serious misunderstanding, unnecessary controversy, and obscure the true issues.

An equilibrium diagram, if it be substantially complete, definitely indicates the number of constituents that can exist in a series of alloys, and also the ranges of composition and temperature in which those constituents may be found as stable phases. Of course, diagrams of this kind do not in themselves establish the precise microscopical formation or appearance that any particular constituent will assume, no matter what treatment it has been subjected to, but viewed in the light of known facts in regard to the relation of structure to the diagrams, an experienced investigator is now in a position to predict, simply by studying the equilibrium diagram, with some confidence the type of microstructure any alloy will show after the most varied treatment.

From the fact that the constitution diagram shows the possible number of constituents of a series, it follows that the many and varied types of structure it is possible to obtain, in steels and other alloys, really correspond to transition stages, and are more or less definitely related to one or, in some cases, two of the constituents that have a place in the diagram. In other words, it is impossible to have more constituents in a micro section than are represented in the diagram, though it may be, and in steels definitely is, possible for those constituents to assume widely different structural forms. It is also a well recognised fact that when these different appearances are observed, they correspond with, and are actually the cause of, certain modifications in the physical and mechanical properties of the particular specimen. On this account some characteristic structural markings have been given names that in some respects convey the idea that they are entities absolutely distinct from the universally accepted constituents. There could be no disputing the necessity of having names for those structures, even though they are merely modified forms of recognised constituents, if they possessed properties sufficiently well defined, but it would unquestionably be advantageous if the selected names, or at least their terminations, were so chosen as to indicate that the substances they denote are transition forms, and if possible, to show their relation to the recognised constituents. To some extent this is now being done by the slow process of evolution and selection. It would, however, be unwise to make any deviation, in a book of this kind, from the names that are now commonly used in steel metallography.

Constitution of Annealed Steels.

At this stage no attempt will be made to define the term annealed as used in the metallurgy of steel, for in some respects the precise meaning implied by that term differs when used by different investigators, and depends upon the previous treatment to which the steel has been subjected. For the present purpose it will be used merely to denote that after rolling or hammering the steel has been heated to about 900° C., kept at that temperature for about an hour, and then slowly cooled to ordinary atmospheric temperatures. In this way the mass slowly cools through the critical points or ranges of temperature, and the constituents take up what may be conveniently regarded as a normal condition. The material is then said to have been "normalised."

Ferrite.—Ferrite is the name applied to iron when it is in the α state. It is the only constituent that exists in pure iron which has been slowly cooled below the Ar_2 critical point (760° C.), and is relatively very soft. It was first microscopically observed by Sorby (1863) in wrought iron. Its micro-structure can be developed by etching in an alcoholic solution of picric or nitric acid, when the outlines of the crystalline aggregates are seen as polygonal grains (fig. 49). There are three possible explanations of the fact that the boundaries of the grains appear dark—*e.g.*, (1) it may be due to a differential etching set up by the interpenetration of the crystal units at the crystal junctions, (2) a differential etching between adjacent crystals of varying orientation, or (3) a selective etching away of the amorphous cement surrounding the crystals.

The internal structure of ferrite was first developed by Dr. Stead, by rather deep etching, when each crystal is seen to consist of a large number of cubical bricks or units (fig. 32). What is known as massive ferrite is a constituent of all carbon steels, containing less than 0·89 per cent. of carbon, that have been slowly cooled. In a fine state of division ferrite is a constituent of all annealed carbon steels. It cannot be definitely stated whether the ferrite of steels is exactly the same as that of pure iron. In all probability it holds a certain limited amount of carbon in solution. Judging from the density and magnetic properties of steels, Benedicks[1] has formed the opinion that the ferrite contained in steels with more than 0·5 per cent. of carbon differs from the ferrite contained in steels of lower carbon content. He concludes that in the former the ferrite holds about 0·27 per cent. of carbon in solution, whilst in the latter the amount of carbon is much less and probably varies with the percentage of carbon contained in the steel. Hence he has given the name "ferronite" to what most other metallurgists describe as ferrite contained in steels with more than about 0·5 per cent. of carbon. It is impossible to say whether this view is correct or not, but if correct, it may be connected with the fact that the whole of the ferrite contained in steels with more than about 0·45 per cent. of carbon is directly deposited from the γ-iron solid solution, whereas, in steels with less carbon, some β-iron is first formed, and then subsequently transformed into α-iron.

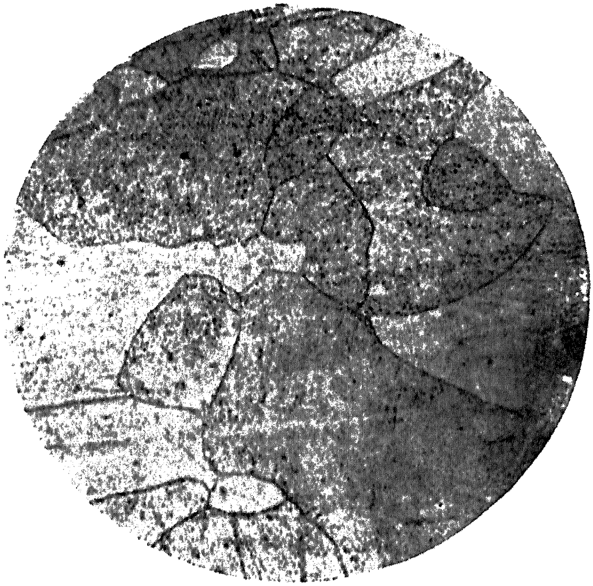


Fig. 49.—Structure of Pure Iron Ferrite (*Carpenter*). × 150.

When etched in picric or nitric acid solutions, the ferrite of steels appears

---

[1] *Recherches Physiques et Physico-Chemiques sur l'Acier au Carbone.*

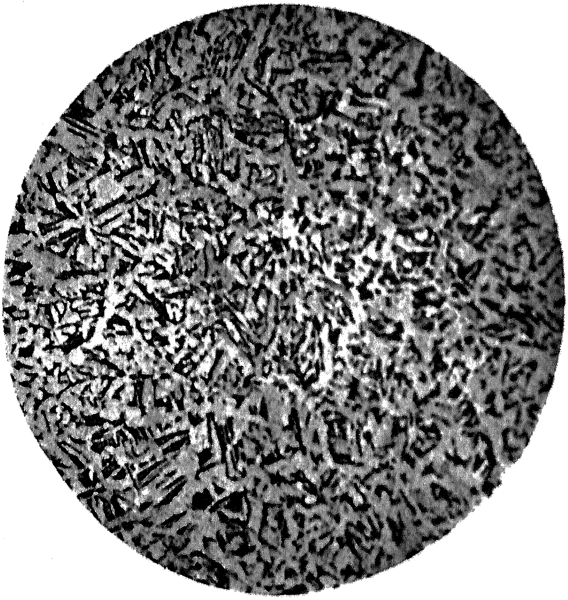


Fig. 50.—0·20 per cent. Carbon Steel. × 150.
Dark areas = Pearlite.
Light ,, = Ferrite.

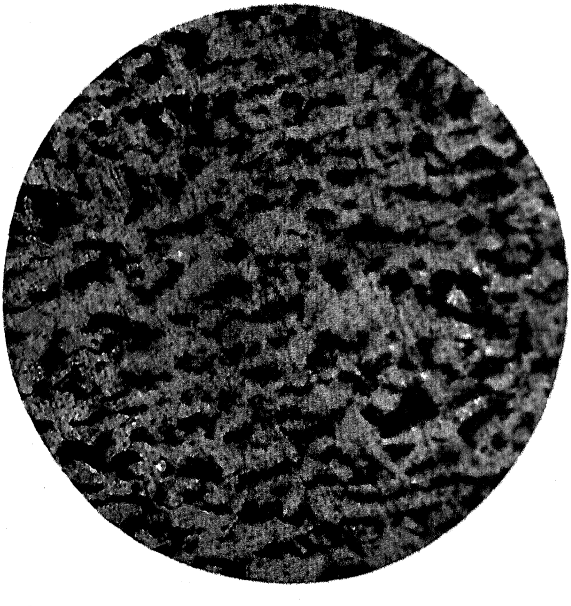


Fig. 51.—0·30 per cent. Carbon Steel. Ferrite and Pearlite. × 150.

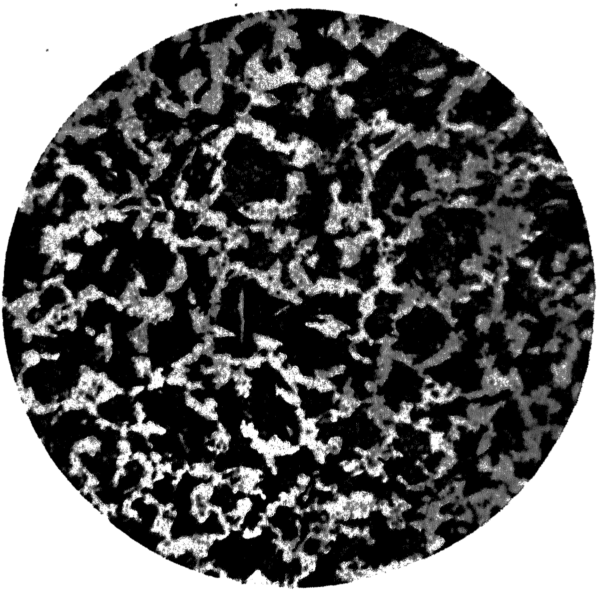


Fig. 52.—0·45 per cent. Carbon Steel. Ferrite and Pearlite. × 150.

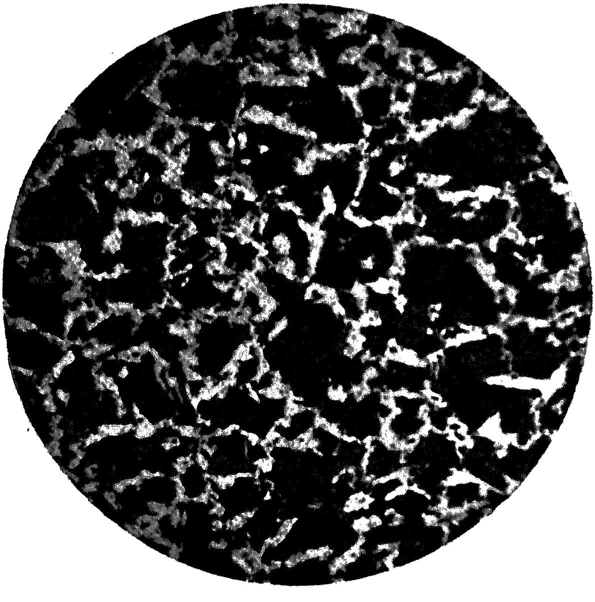


Fig. 53.—0·60 per cent. Carbon Steel. Ferrite and Pearlite. × 150.

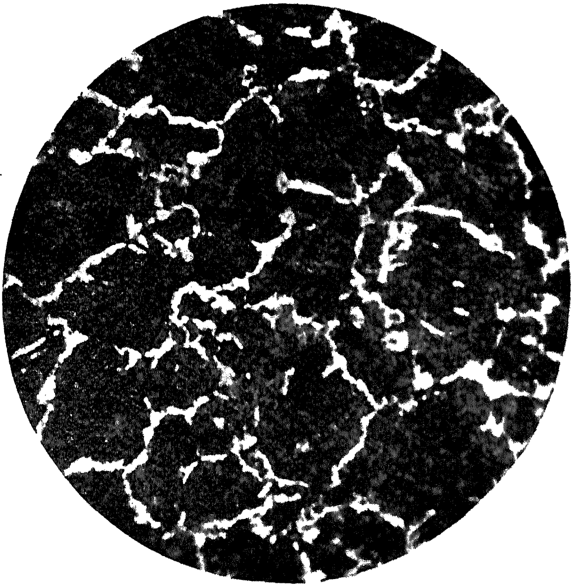


Fig. 54.—0·75 per cent. Carbon Steel. Ferrite and Pearlite. × 150.

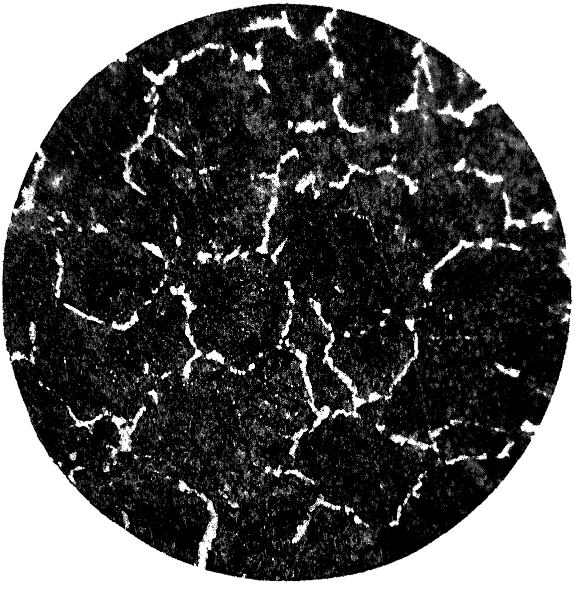


Fig. 55.—0·85 per cent. Carbon Steel. Ferrite and Pearlite. × 150.

almost white. It is shown in figs. 50, 51, 52, 53, 54, and 55 as white areas in steels containing respectively 0·20, 0·30, 0·45, 0·60, 0·75, and 0·85 per cent. of carbon.

In many steels containing elements other than iron and carbon, the ferrite may retain some of the added element in solid solution, and its properties would accordingly be modified. Even in cases of this kind it is customary to refer to the relatively pure iron as ferrite.

Cementite.—Carbide of iron or cementite (Fe_3C) is the only chemical compound of iron and carbon that has been definitely isolated from annealed carbon steels. This constituent was first seen under the microscope by Sorby (1863), and is exceedingly hard and brittle. It is strongly electro-negative to ferrite, and in specimens containing the two constituents, when etched in nitric or picric acid solutions, it is left practically unattacked (see fig. 56). Cementite is present in all slowly-cooled steels. In those containing less than 0·89 per cent. of carbon it exists as irregular-shaped laminated plates along with ferrite, whilst with higher percentages of carbon it is present in the massive form, and is seen under the microscope as a white matrix surrounding areas which are dark when the specimens have been etched with nitric or picric acid solutions. The thickness of these cementite boundaries increases with the carbon content.

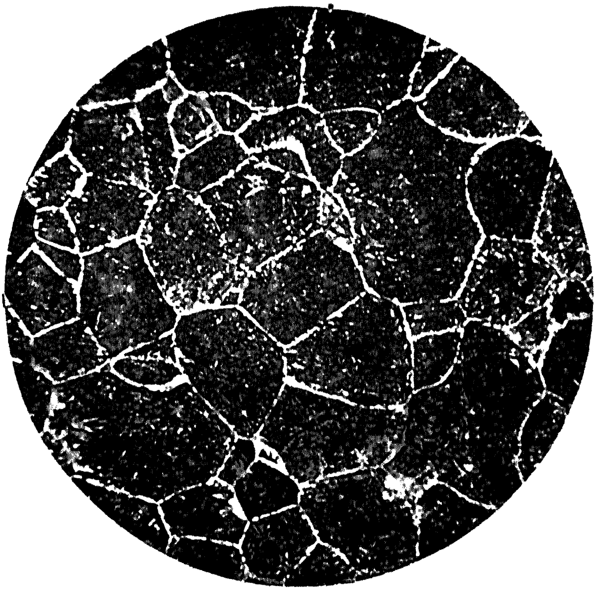


Fig. 56.—1·20 per cent. Carbon Steel. × 150.
Dark areas = Pearlite.
Light „ = Cementite.

Strictly speaking, ferrite and cementite are the only definite constituents of slowly-cooled carbon steels, and these are respectively represented in the equilibrium diagram by the vertical lines A B F and H J (fig. 57). When these two constituents are associated together they give rise to a number of characteristic and more or less regular microstructures, which practically determine the actual physical properties of the mass. It is, therefore, both convenient and necessary that these appearances should have names by which they can be described, but whether these names should terminate with "ite" or "itic" is a matter of opinion. It is of very little consequence so long as no misunderstanding arises as regards the actual meaning of the terms.

Messrs. Campbell and Kennedy[1] have published evidence which seems to indicate that a carbide of iron, Fe_2C, is also present in mixtures containing high percentages of carbon. They are of the opinion that this compound separates from γ-iron solid solutions containing more than about 1·0 per cent. of carbon. Prolonged annealing at moderately low temperatures (say just below 700° C.) brings about the decomposition of cementite with the formation of ferrite and graphitic carbon. This reaction occurs even at higher temperatures in pure iron-carbon steels containing more than 0·89 per cent. of carbon. Thus Arnold has shown that after annealing a 1·47 per cent. carbon steel at 1,000° C. for 72 hours followed by slow cooling, it contained 1·14 per cent. of free or graphitic carbon. Steels with less than 0·89 per cent. of carbon do not behave in this manner on annealing at 1,000° C., which is no doubt due to the carbon being in solution at that temperature. The pronounced decomposition by annealing at 1,000° C., as indicated by

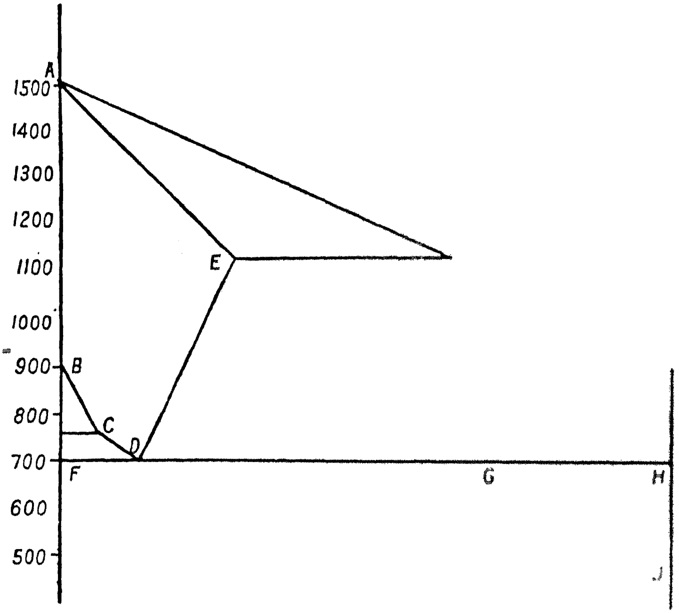


Fig. 57.

---

[1] *Journ. of the Iron and Steel Inst.*, 1902, No. 2.

Arnold's experiments, is probably due to the fact that with 1·47 per cent. of carbon some of the carbide still remains in the free or undissolved condition, and is thereby more readily decomposed at the high temperature. The free carbon thus formed then accelerates the rate at which the carbide (which subsequently falls out of solution as the mass cools) breaks up into its constituents.

Pearlite.—Pearlite was the term introduced by Sorby (1863) for the pearly areas of an etched annealed carbon steel. Although metallographers agree, both as regards the utility of this term (which implies that it is a definite constituent) and the constitution of the structural appearance to which it is applied, it is necessary to note that pearlite is not a simple constituent. The dark pearlite areas in figs. 50 to 55 consist of two constituents, ferrite and cementite, usually arranged in lamellæ, in the proportion represented by the eutectoid point D (fig. 57). These areas correspond with that part of the steel which contained 0·89 per cent. of carbon in solid solution immediately before the Ar_1 change occurred. The excess of ferrite in steels containing less than 0·89 per cent. of carbon separates, on cooling, at the temperatures indicated on the line B C D, whilst the excess of carbon in steels containing more than 0·89 per cent. is similarly deposited at temperatures on the line D E. Hence the curves B C D and D E are really temperature-solubility curves, which indicate respectively the solubility of iron on the one hand and of carbide of iron on the other, in the solid solution.

In all cases, therefore, it is evident that the percentage of carbon in solution just before the Ar_1 change takes place is 0·89, corresponding with the point at which the two solubility curves intersect each other. Further, as pearlite is produced by the simultaneous deposition of ferrite and cementite from the eutectoid solid solution, at the temperature of the Ar_1 change, it follows that the field of a true pearlite area contains exactly the same amount of carbon—viz., 0·89 per cent.

Pearlite etches dark both in the presence of massive ferrite and of cementite, owing to the relatively fine state of division of its constituents, which cause the electrolytic action of the etching solutions to be concentrated thereon.

The granulation of pearlite and of its two constituents varies between the infinitely fine and the excessively coarse. From the very nature of its origin and constitution this is precisely what would be expected. It is formed as a result of the decomposition of a homogeneous solid solution at the temperature of the Ar_1 point. Just before that change the iron is in the γ state, when it and the iron carbide are capable of mutually holding each other in solution. The disintegration of this solid solution takes place at one temperature throughout the whole mass, and is completed in a relatively very short time. Immediately below the Ar_1 point, and after the inversion is complete, the mass consists of α-iron and carbide of iron, but at the initial stage of separation they are in such an exceedingly fine state of division that, if by any means they be kept in that condition—*e.g.*, by suddenly cooling the mass—the grain of the two constituents would be ultra-microscopic. If, however, the mass be kept at a temperature just below the Ar_1 point, the fine particles of cementite coalesce, as do the particles of ferrite, first forming very thin alternate plates of the two constituents. If the time be prolonged these plates become thicker, and finally the cementite becomes isolated in large patches surrounded by ferrite crystals. Between the two extreme forms almost any degree of fineness can be obtained by suitably varying the conditions in regard to time and temperature. Under normal conditions the pearlite of steels containing less than the eutectoid percentage of carbon is rather finely laminated (see dark areas of photos., figs. 50 to 55). In steels containing more carbon the pearlite is usually of a coarser character (see photos., figs. 58 and 59).

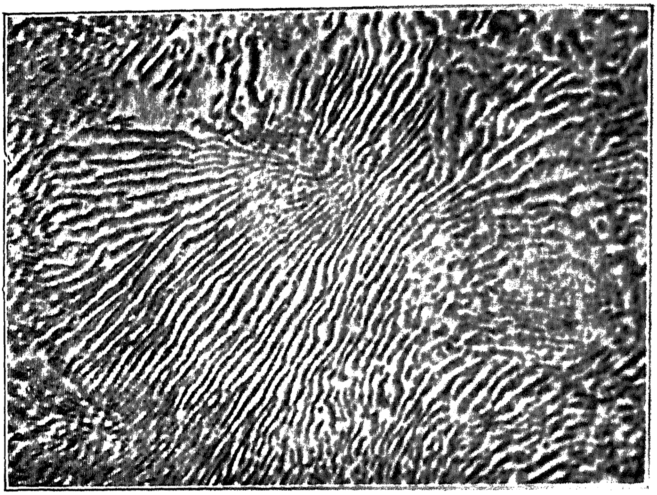


Fig. 58.—Pearlite (*Osmond*). 1,000.

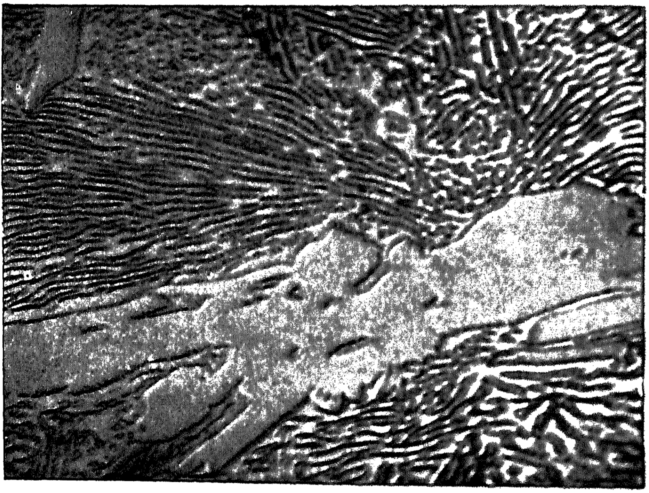


Fig. 59.—Pearlite and Cementite. 1·57 per cent. Carbon (*Osmond*). × 1,000

From what has been said, it will be readily understood that pearlite is not a true constituent, but a characteristic appearance of two totally different constituents when associated together. Pearlite may be represented in the equilibrium diagram (fig. 57) by the eutectoid point D, or as existing inside the area F G H J.

Sorbite or Sorbitic pearlite is a finer form of pearlite, which may be regarded as the transition stage between **troostite** or troostitic pearlite and normal pearlite. Its appearance under high magnification is shown in fig. 60.

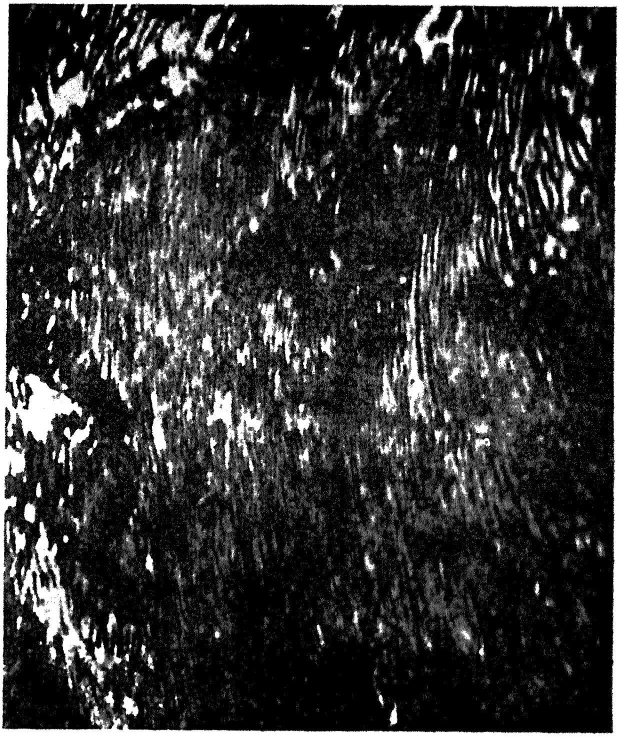


Fig. 60.—Sorbitic Pearlite (*Osmond*). × 1,500.

Constitution of Quenched Carbon Steels.

It is now necessary to describe the constitution and structure of steel at temperatures higher than that of the ordinary atmosphere, and the changes that occur with varying temperatures and varying rates of cooling from those temperatures.

In the previous sections it was pointed out that there are marked breaks or discontinuities in the thermal properties of steels at certain temperatures which correspond with internal molecular or intercrystalline changes.

Directly to determine the nature of these changes by microscopically observing a prepared section of the metal while passing through the critical temperature is a problem that has not yet been successfully solved. Hence the methods in use for ascertaining the alteration of structure that accompanies these thermal arrests are all more or less indirect. The method in most general use for ascertaining the type of structure possessed by a metal at any given temperature is to heat a small section to the desired temperature, and after allowing sufficient time for equilibrium to be established, rapidly to cool it by quenching in ice-cold water or any other suitable medium. The validity of this method depends upon the assumption that the constitutional changes through which the alloy would pass with slow rates of cooling are suppressed, and the structure and constitution it then possessed are thereby retained, and can then be examined under the microscope. The theoretical explanation of the process is as follows :—

With quick rates of cooling the temperature at which an inversion takes place is lowered; the general term applied to this lowering is supercooling; as the rate of cooling increases the degree of supercooling increases, and also the velocity of the inversion, until a certain rate is reached, when the velocity is at a maximum. After this condition has been reached the velocity quickly diminishes with the increased rate of cooling, and with sufficient supercooling may actually become zero. With such conditions as regards quenching rates, the suppression of an inversion would be complete, and the constitution of the metal after quenching would be the same as when it was above the normal temperature of the inversion. It would then be what is sometimes described as "stereotyped." It is, however, necessary to recognise the important fact that, although the physico-chemical constitution prevailing at the high temperature can be retained down to the ordinary temperature by this means, it frequently happens that the appearance as seen under the microscope is remarkably different. In other words, a difference of structural markings does not necessarily indicate a difference of constitution. It ought to be noted here that there are undoubtedly some thermal critical points that have not so far been suppressed, even with the most drastic quenching yet adopted. There is every reason for considering that the Ar_3 and Ar_2 points in pure iron belong to this class.

The so-called constituents or structural appearances that have been observed in polished sections of steel that have been previously quenched are known by the following names :—

1. Martensite or Hardenite.
2. Austenite.
3. Troostite or Troostitic pearlite.
4. Sorbite or Sorbitic pearlite.

Martensite and Austenite.—For many reasons these two constituents may most conveniently be considered at the same time.

Martensite.—This term is used for a special type of structure, which is obtained by quenching carbon steels containing up to 1·0 per cent of carbon from temperatures above their highest recalescence point, when the whole of the carbide of iron is in solid solution. When properly quenched from these temperatures the etched surfaces of the steels are found to have

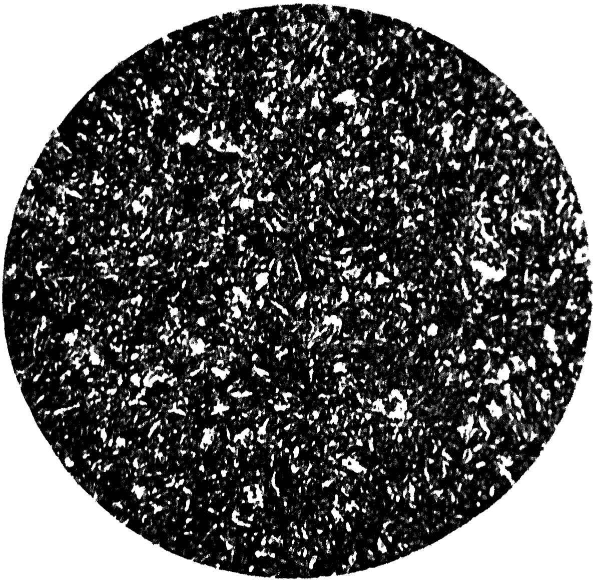


Fig. 61.—Quenched Carbon Steel. Martensite. × 150.

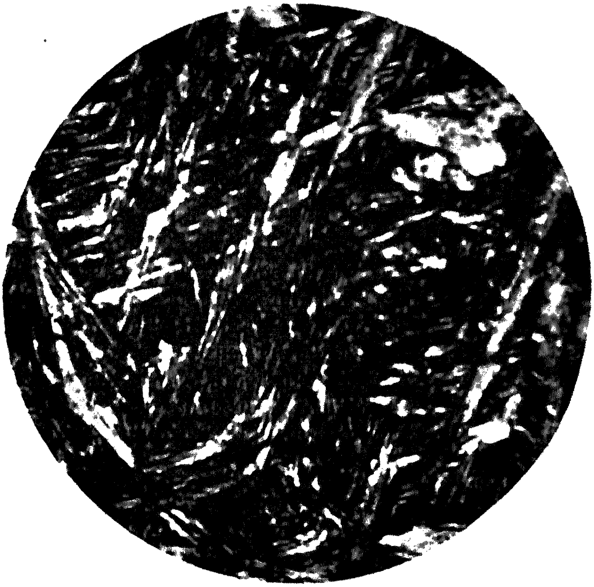


Fig. 62.—Quenched Carbon Steels. Martensite. × 1,000.

what is frequently called an acicular or interlacing needle like structure, the markings of which are often disposed in triangular formation (see figs. 61 and 62). From the fact that small sections of steels containing less than 1·0 per cent. of carbon, when suitably quenched, present only this acicular martensitic structure, it follows that these markings are in some way related to the solid solution of carbide of iron in γ-iron. The hardness of steels that have been quickly quenched and are entirely martensitic varies considerably, and depends almost exclusively upon the percentage of carbon they contain. With low percentages of carbon the martensitic constituent is relatively very soft, but with about 0·90 per cent. of carbon it is an intensely hard substance and easily scratches quartz. Martensite is magnetic.

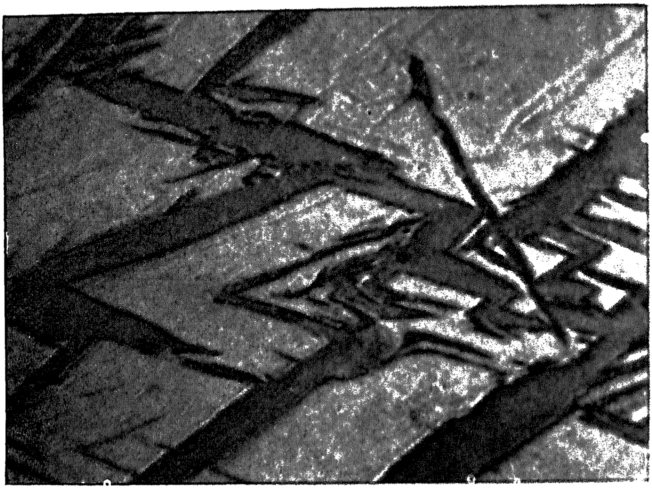


Fig. 63.—Quenched 1·57 per cent. Carbon Steel (*Osmond*) × 1000

White Areas = Austenite.
Black ,, = Martensite.

Austenite.—This constituent can only be obtained in carbon steels containing upwards of 1·0 per cent. of carbon by very rapid quenching from temperatures above 1,000° C. With pure carbon steels it has never been obtained in a pure state; it is always associated with more than 30·0 per cent. of martensite. In the presence of martensite, austenite usually remains white after etching. It is generally considered to be non-magnetic. The white areas in fig. 63 correspond with austenite, and the dark with martensite.

As regards the true constitution of martensite and austenite, opinions are very much divided. The chief points of the many suggestions that have been made are given below :—

1. (Osmond and others) a solid solution of carbide of iron in iron in which the iron is partly β and partly α.

2. (Le Chatelier) a similar solid solution, but the iron is chiefly in the α state.

3. (Benedicks) a solid solution of β-iron.
4. (Arnold) a compound having the formula $Fe_{24}C$.
5. Twin crystals of the γ-iron solid solution.

In regard to Nos. 1 and 3, it may be pointed out that they do not appear to be of any value, nor do they seem to have any support from theoretical reasons or experimental facts.

As regards No. 4, there is no doubt that the eutectoid steel containing 0·89 per cent. of carbon corresponds with the formula $Fe_{24}C$, but that alone cannot be regarded as proving the existence of such a compound. Many eutectics of metallic systems possess compositions that correspond with chemical formulæ, although it is not usual to regard them as being necessarily definite compounds. It must, however, be admitted that both eutectics and eutectoids may ultimately be found to be in a kind of loose chemical combination, which are only capable of existing in the liquid or in the solid states respectively above their particular critical temperatures. Be that as it may, it does not affect the question of the constitution of martensite obtained at ordinary temperature by quenching steel from high temperatures. The real point to decide, if possible, is whether the martensitic markings are formed as a result of a partial decomposition of the pre-existing solid solution with the consequent formation of a certain amount of α-iron, or whether they are due to some other cause.

In this connection there are certain fundamental matters of theory which ought to be carefully considered before drawing conclusions from the actual facts. These are :—

1. Is the process of very rapidly quenching—*e.g.*, a small section of a steel containing 0·9 per cent. of carbon, by almost instantaneous immersion whilst at a temperature of about 900° C., in ice-cold water—sufficient completely to suppress the Ar_1, the carbide change, and thereby to secure that the specimen shall retain the constitution it possessed at the higher temperature ?
2. What is the cause of the characteristic acicular markings ?
3. Is martensite microscopically homogeneous ?
4. Why is a quenched steel consisting entirely of martensite always magnetic ?

Before attempting to answer these questions, it will be well briefly to study a series of alloys that are in many ways analogous to carbon steels. By doing this the subject can be criticised in a broader light, and the evidence obtained, though only of a circumstantial character, may be advantageously considered in framing answers to the above questions. The alloys of copper with aluminium containing from 9 to 16 per cent. of aluminium undergo very similar changes, both thermally and structurally, to the carbon steels; moreover, the structure of these alloys after they have been quenched from temperatures above the thermal transformations is practically identical with that of martensite in quenched carbon steels. That part of the constitutional diagram which corresponds with the particular aluminium-copper alloys under consideration is represented in fig. 64. At temperatures inside the β area the alloys consist of a homogeneous series of solid solutions, which are analogous to the γ solid solutions of the iron-carbon system. On cooling, these solid solutions pass through changes that are essentially of the same nature as those of steels. At the temperatures on the line A B α crystals that are relatively rich in copper separate from the β solid solution in exactly the same way as practically pure iron is deposited from solution at temperatures on the line B C D, fig. 57. With alloys containing more than 12·4 per cent. of aluminium—that is, those which fall to the right of the eutectoid point B, fig. 64—γ crystals relatively rich in aluminium separate from solution at temperatures on the line B C in a similar manner to the separation of carbide of iron at temperatures on the line D E, fig. 9. In all cases as the temperature falls the composition of the β solid solution approximates progressively to that of the eutectoid point B, and when the temperature of the line D B E, 560° C., is reached, it corresponds exactly with that

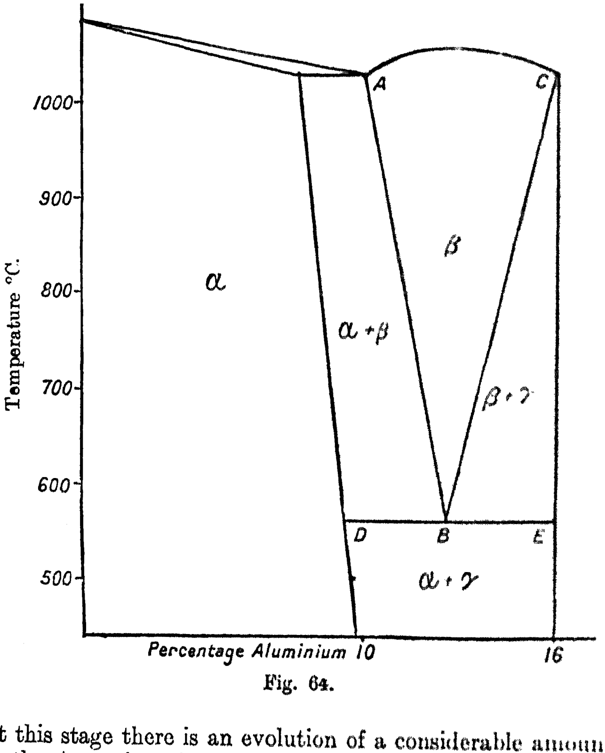


Fig. 64.

point. At this stage there is an evolution of a considerable amount of heat, similar to the Ar_1 point of carbon steels, and the β constituent breaks up bodily into α and γ. Thus, in both series of alloys, the solid solutions undergo exactly the same type of thermal and constitutional changes. The structure of a slowly-cooled alloy containing 10·0 per cent. of aluminium is shown in fig. 65. The same alloy, after it has been quenched from above the temperature of the line A B, fig. 64, gives a structure shown in fig. 66. This interlacing acicular structure is almost identically the same as the martensitic markings of a quenched carbon steel. When it is remembered that from a physico-chemical standpoint these two series of alloys are analogous,

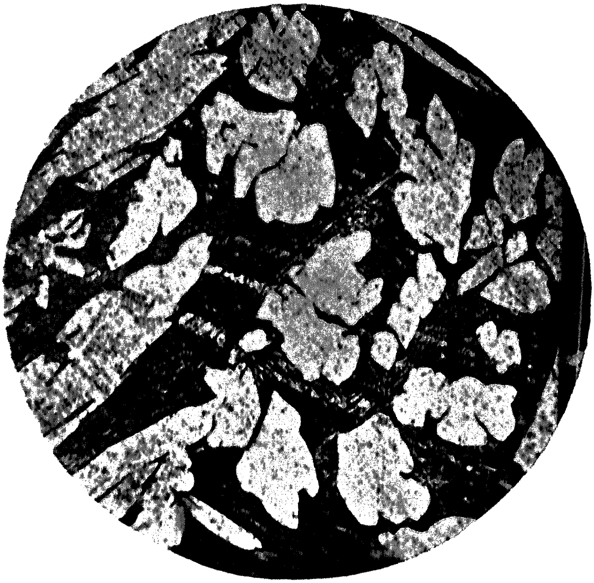


Fig. 65.—Slowly cooled. × 150.

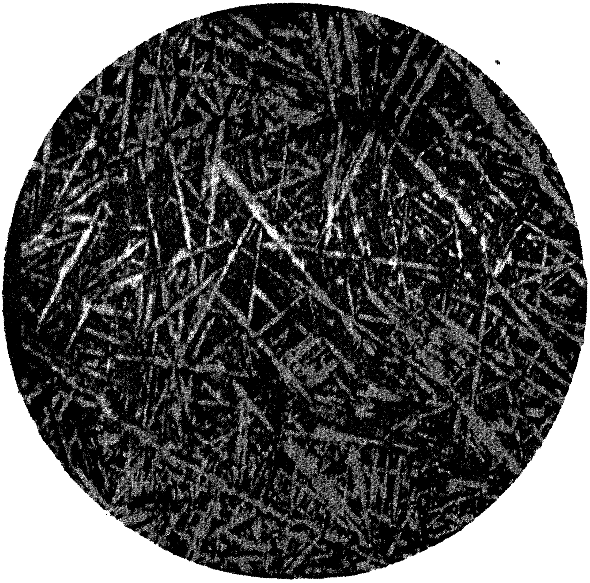


Fig. 66.—Quenched from 900° C. (*Carpenter* and *Edwards*). × 150.

Copper = 90·0 per cent.
Aluminium = 10·0 ,,

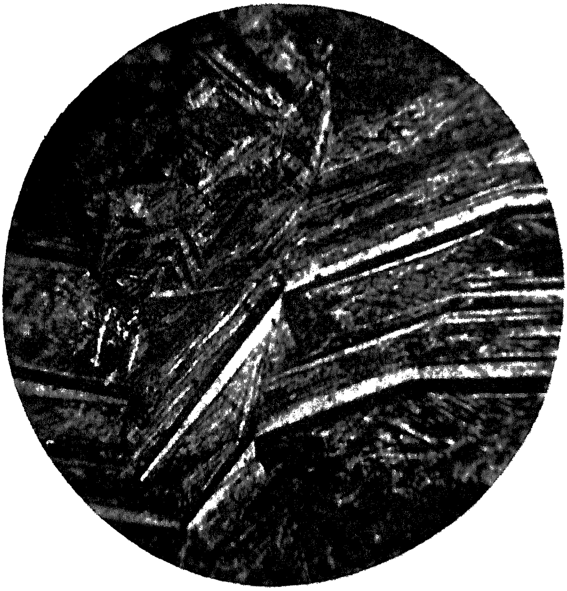


Fig. 67.— × 150.

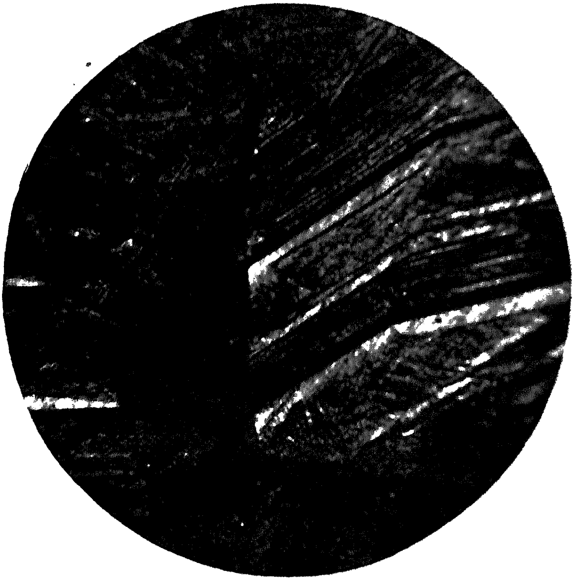


Fig. 68.— × 150.

Figs. 67 and 68.—Twin Crystals produced by Quenching. Same Area taken under Oblique Light at Different Angles (*Edwards*).

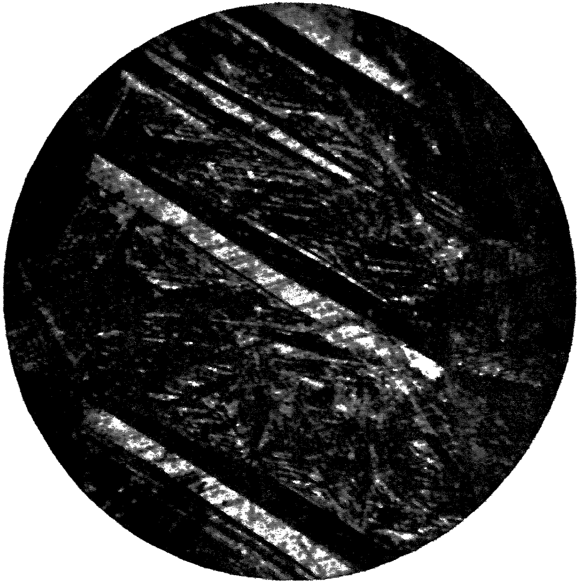


Fig. 69.— × 250.

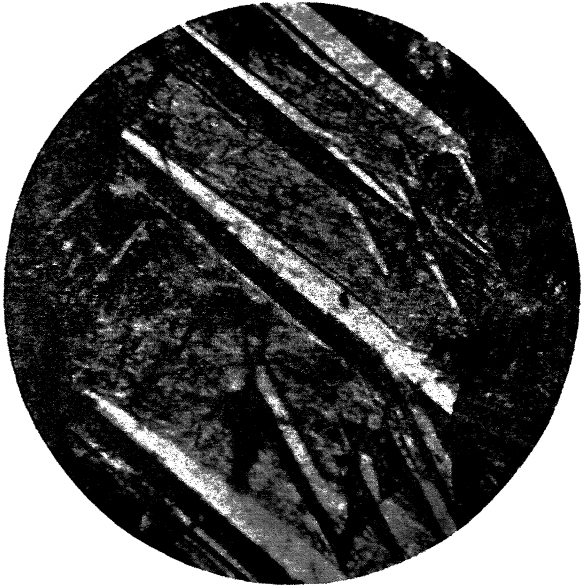


Fig. 70.— × 250.

Figs. 69 and 70.—Twin Crystals produced by Quenching. Same Area taken under Oblique Light at different Angles (*Edwards*).

the structural resemblance of the quenched specimens is not very surprising. In the case of the non-ferrous alloys, no difficulty has been experienced by metallographers in arriving at a general understanding as to what such a kind of structure should be called. They simply describe it as the β constituent, which, strictly speaking, means that it is the type of structure peculiar to the alloys that have been quickly quenched from temperatures at which the β constituent was stable. This kind of nomenclature is absolutely non-committal, yet it conveys a definite and accurate idea of the treatment to which the specimen has been subjected, and is a safe foundation upon which to graft future experimental facts. Further, in the particular instance cited, it has recently been proved that this procedure is indeed wonderfully accurate. For many years the acicular structure was universally spoken of as the β constituent, without any serious question being raised as to why this apparently duplex structure was always produced and still regarded as one constituent. It was suggested by the author[1] that this apparently duplex structure was due to the solid solution crystals which are homogeneous and individually of uniform orientation at the temperature from which they were quenched, becoming split up into many twin crystals by the strains that are set up in the quenching process. At a later date[2] the author proved that the light and dark markings were indeed caused by prolific crystal twinning, and that these quenched specimens, although seemingly hetrogeneous, are actually homogeneous.

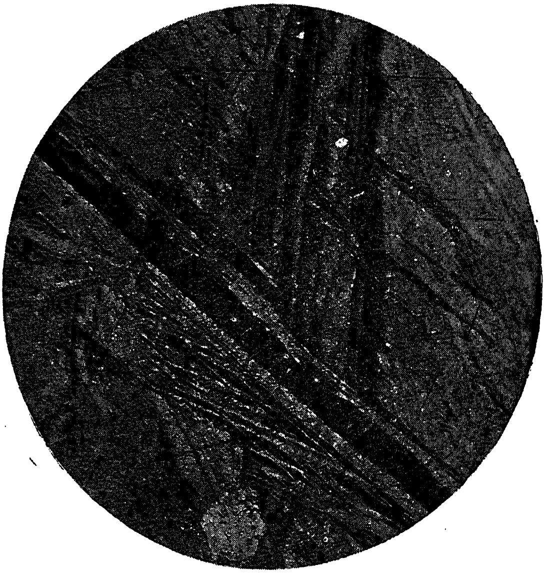


Fig. 71.—(*Carpenter* and *Edwards*). × 150.

---

[1] *Journ. Iron and Steel Inst.*, 1910, No. 2.
[2] *Zeitschrift für Metallographie*, No. 1, 1913.

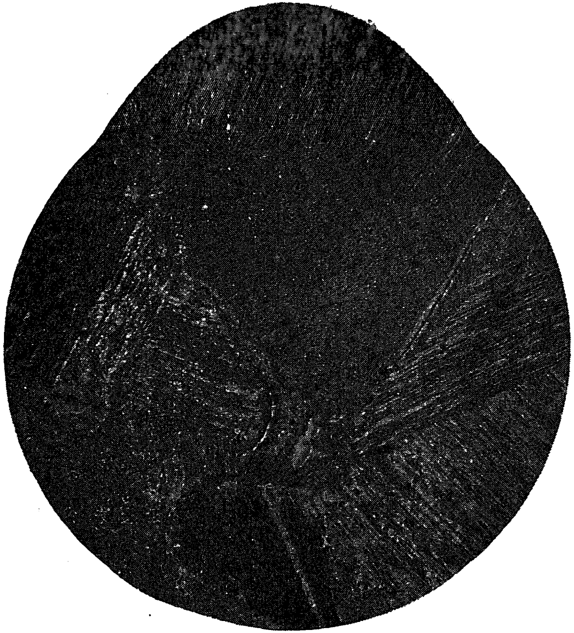


Fig. 72.—Vertical Light. × 150.

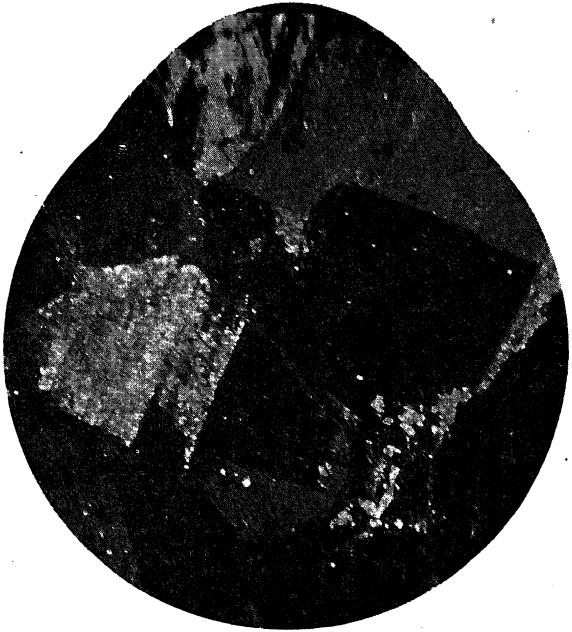


Fig. 73.—Oblique Light. × 150.

Figs. 72, 73, and 74.—Same Area of Martensite taken under different Illumination (*Edwards* and *Carpenter*).

Figs. 67 and 68 were taken from the same area by the use of oblique light with the source of light differing in the two cases by about 180°. In this way it will be noticed that the various light areas become dark and *vice versâ*, which clearly demonstrates that the degree of lighting can be varied at will, as it is merely due to the angle at which the rays of light strike the numerous twinned facets, of which the crystal grains are composed.

Those copper-aluminium alloys, which fall to the right of the eutectoid point B, fig. 64, when quenched from high temperatures, also show a microstructure which is remarkably like that of the austenite and martensite of quenched high carbon steels (see photo., fig. 71), and compare with that of fig. 63. This also has been shown to be due to crystal twinning (see figs. 69 and 70).

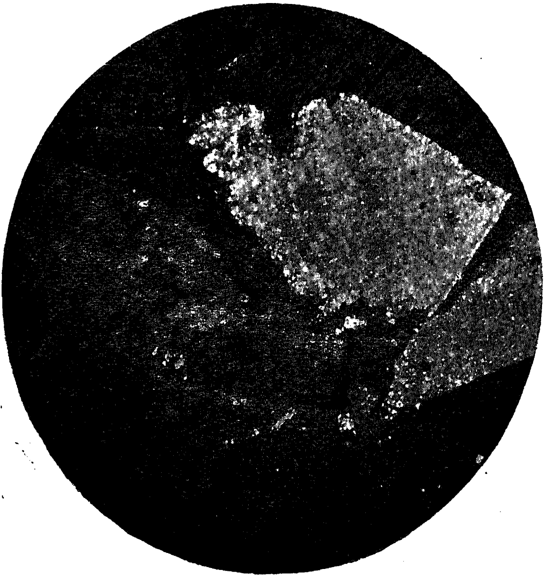


Fig. 74.—Oblique Light. × 150.

Judging from analogy, it is, therefore, quite natural to expect that the operation of quenching carbon steels will bring about pronounced crystal twinning, and that the acicular markings of martensite are connected with this twinning. As shown by Prof. Carpenter and the author,[1] this expectation has been justified, and from figs. 72, 73, and 74 there can be no doubt that martensitic markings are caused by crystal twinning. As to whether there is also a certain quantity of α-iron present in martensite, it is at present unsafe to make any definite conclusion. The presence of α-iron would account for the magnetic properties of martensite, but, on the other hand, these magnetic properties do not definitely indicate the presence of α-iron. It has been suggested by Prof. Carpenter and the author that the magnetic properties of martensite may be due to the formation of amorphous layers upon the surfaces of slip or twinning produced by quenching.

---

[1] *Journ. Iron and Steel Inst.*, No. 1, 1914.

Before going any further into this question, it will be well to give a brief account of the work that has been done regarding the constitution of austenite.

1. Osmond first demonstrated that a 1·6 per cent. carbon steel quenched in ice-cold water contained about 60 per cent. of white austenitic areas (fig. 63), and that, according to the scratch test, a specimen of this kind was slightly softer than a quenched 0·9 per cent. carbon steel containing only the martensitic constituent.

2. The same investigator found that by cooling in liquid air an austenitic *plus* martensitic steel, the austenitic areas become transformed into martensitic areas, and as a result the magnetic intensity of the mass was increased.

3. After stating that there is not a single cause for assuming a different empirical composition between the martensitic and austenitic areas, and that the difference in their properties is due to γ-iron being the phase present in the latter, and (probably) β-iron in the former, Benedicks[1] says:—

"If one examines a specimen with this characteristic structure, one really is led to ask, What is the reason that the specimen does entirely pass over into martensite if martensite corresponds better to the thermal equilibrium on quenching; or, on the other hand, that it does not remain as austenite, if austenite corresponds with the thermal equilibrium on quenching? Certainly the dissolved carbon has a very large influence on the preservation of the mixed crystals as austenite, but, on account of its even distribution, this influence must necessarily be the same throughout.

"The answer to this question would not appear to require much seeking. It was first shown by Osmond that martensite, which has been formed from austenite by cooling in liquid air, has a larger volume than the austenite (standing in relief on the previously plane surface). Further, the dilatometric work of Le Chatelier, and of Charpy and Grenet, has shown that the transformation from γ to β (as well as to α) iron is accompanied by dilatation. These two facts clearly demonstrate that the passage from austenite to martensite is accompanied by a considerable increase of volume. It is obvious that the pressure necessarily resulting from the increase of volume at the transformation from austenite to martensite must have an extremely important influence. Already by the cooling of the outer portions of the specimen the interior must be subjected to a high pressure (even if here the γ state steel exists exclusively. When, further, a portion of these γ crystals in the interior is transformed into martensite, this must result in a considerable increase of the pressure. The transformation of austenite into martensite cannot, therefore, go on beyond a certain limit, where the increase of pressure (corresponding to the increase of volume) will put a stop to further transformation of the γ crystals. So these crystals will be preserved as austenite in their non-magnetic state at ordinary temperatures."

The above quotation constitutes an excellent summary of the views held by Benedicks and others as regards the constitution of austenite, and to some extent of martensite.

Some of the more important points in favour of the idea that martensitic and austenitic areas are twinned crystals of the same constituent are included in the following quotation from a paper by Carpenter and the author :—

---

[1] *Journ. Iron and Steel Inst.*, 1908, No. 2, p. 273.

"The fact that the so-called austenitic areas of quenched carbon steel appear to change into what are regarded as martensitic areas when immersed in liquid air, is quite consistent with the idea of twinning, because the extra strain put upon the mass would cause further twinning, particularly in those areas (austenitic) which had previously escaped this change. It is also of some importance to note that the relief patterns produced on polished specimens that have been cooled in liquid air do not necessarily indicate that there has been an actual increase in volume, for, as a matter of fact, exactly the same kind of relief forms are produced when previously polished specimens of the copper-aluminium alloys, already referred to, are quenched from temperatures above their highest critical point, but the specimens so treated actually occupy a smaller volume than if they were slowly cooled. Even if it is found that these specimens occupy a slightly larger volume than before being cooled in liquid air, it would agree with the facts relating to the change from the crystalline to the amorphous condition, because Beilby has shown that this is accompanied by an increase in volume.

"As regards the non-existence of austenitic areas at the surfaces of a quenched steel, it may be pointed out that exactly the same applies to areas of similar appearance in the copper-aluminium alloys. We have repeatedly noticed that in these alloys very quick quenching rates produce thin twin lamellæ (like martensitic areas), whereas with slower quenching velocities the same sized specimens would show much larger twins (corresponding to austenite). This is rather a significant fact, in view of what has been said about the increased pressure of martensitic areas at the surface preventing the austenitic transformation in the interior. If the retention of austenite is in any way due to the pressure of the martensitic areas, then it ought to be possible to obtain almost pure austenite in certain parts of the specimen by arranging to produce a positive pressure in the interior of the mass as well as on the outside. Thus, by allowing the carbide change to take place in the central part of a specimen, the increased volume which would then occur in that area would exert a kind of back pressure upon the untransformed material surrounding it. Hence, as it is possible to obtain from 60 to 70 per cent. of the austenitic areas without any of the carbide change having taken place in any part of the mass ; if the pressure of the martensitic areas is the cause of the retention of the austenitic areas, it ought to be possible to obtain much more of the latter when both these pressures are operating in the same direction. Up to the present it has not been possible to produce in any part of a quenched carbon steel more than about 70 per cent. of the austenitic areas. This is a very significant fact, for if the effect is due to crystal twinning, it can never be possible to obtain a purely austenitic carbon steel at the ordinary temperature, even with the quickest possible rates of quenching. In the present state of knowledge, therefore, we are of the opinion that there is not a single fact which proves that there is any difference whatever in the constitution of martensitic and austenitic areas, and, further, that no facts can be advanced in support of that view, which are not also quite as readily explained by the view that the effects are due to crystal twinning. On the other hand, whilst it has not yet been definitely established that the martensitic areas are really twin crystals of austenite, this view is not only rational, ut is supported by the facts relating to other alloys which are of the same hysico-chemical nature."

Dr. Benedicks has made some interesting observations upon the electrical roperties and specific volumes of quenched steels (see fig. 75). He has shown hat the electrical resistance of troostite, which is the first product resulting rom the decomposition of the slowly-cooled γ-iron solid solution, is the ame as that of pearlite. Further, the specific volume—that is, the volume ccupied by 1 gramme of steel—is the same for pearlite and troostite. When artensite is formed by quenching from high temperatures, the electrical esistance and specific volume are raised very considerably above that of troostite. As regards the specific volumes, these facts are rather significant. For example, it has been demonstrated by Le Chatelier and by Charpy and Grenet that the transformation on cooling through the Ar_1 change, corresponding with the formation of troostite from the γ-solid solution, is accompanied by a marked increase of volume. This definitely indicates that troostite occupies a greater volume than the solution from which it is formed. Troostite may, therefore, be taken as representing the condition with the highest specific volume for slow rates of cooling. Since, however, martensite, which is obtained by quenching, has a greater volume than troostite, it also follows that it must have a larger volume than the initial solid solution. Hence, it is natural to conclude that martensite cannot be of the same

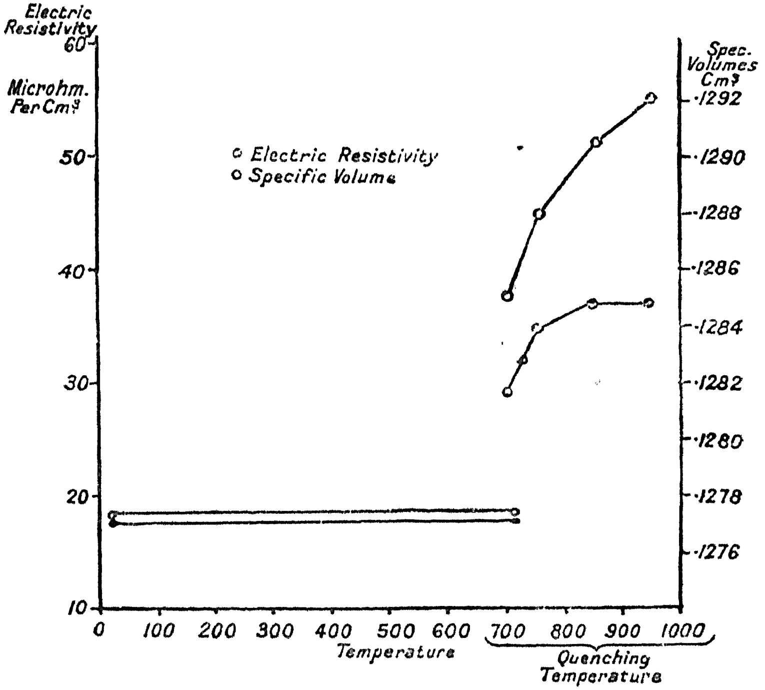


Fig. 75.—(*Benedicks*).

physico-chemical constitution as troostite, because a variation in the size of crystal in the latter case does not give rise to a change of volume. The explanation which appears to fit in with the facts, and is in agreement with other theories, is that martensite corresponds to the γ iron solid solution, which has been very severely strained in the quenching, and that this deformation increases the volume in the same way as cold working of metals.

Troostite.—This constituent was first discovered by Osmond,[1] who named it in honour of the French chemist, Troost.

Troostitic areas in specimens rapidly become black when placed in etching solutions, and on this account its presence can be frequently detected without a microscopic examination. When viewed under the microscope it appears as dark furled-like areas, as seen in figs. 76 and 77, which Osmond described as nearly amorphous, and slightly granulated. Troostite can be obtained in almost any steel, no matter what the carbon content, by modifying the temperature from which the specimens are quenched, or the rate of the quenching. It can also be obtained by heating martensite or austenite to 400° C., or cooling to the temperature of liquid air.

Originally Osmond considered troostite to correspond to some transitory association between β-iron and carbon. Arnold[2] describes it as emulsified carbon present in an exceedingly fine state of division in tempered steels; and Roberts-Austen's[3] definition was practically the same. Le Chatelier[4] says:—Troostite is probably a solid solution, differing from martensite and austenite in being magnetic at its temperature of formation. Boynton[5] formed the opinion that troostite was a form of carbonless iron, and as its properties, particularly its black colouring on etching, differ so much from α-iron, he concluded that it was β-iron. Almost immediately after Kourbatoff[6] showed that Boynton's views were untenable, and suggested that troostite was a solution of elementary carbon in iron. This idea was, however, refuted by Benedicks,[7] who holds that everything we now know points to the fact that Osmond quite correctly defined troostite as an intermediate form between martensite and pearlite. Between troostite and pearlite there is a continuous transition, and one is naturally led to the conclusion that troostite is a pearlite with ultra-microscopically small particles of cementite, and that the iron is in the β or α state. In addition, Benedicks made a most interesting suggestion to the effect that troostite offers, in the domain of alloys, an interesting analogy to colloid solutions. Considered in the light of more recent researches, this colloid theory has had great support, though it must be mentioned that later writers have expressed the same idea in somewhat different language. In a very valuable piece of work, in which many new facts are brought to light, M'Cance[8] concludes (1st) that troostite consists essentially of α-iron which is in the amorphous condition, or which has not yet attained its crystalline state of ferrite, and (2nd) that troostite contains carbon in suspension, and not in solution, as

---

[1] *Bulletin de la Société d'Encouragement pour l'Industrie Nationale.*
[2] *Proc. Inst. Civil Engs.*, vol. cxxiii., 1895-6, Part I.
[3] *Proc. Inst. Mech. Engs.*, 1899, p. 35.
[4] *Bulletin de la Société d'Encouragement*, 1900, p. 661.
[5] *Journ. Iron and Steel Inst.*, 1904, No. 2, p. 262.
[6] *Revue de Métallurgie*, Feb., 1905, p. 169.
[7] *Journ. Iron and Steel Inst.*, 1905, No. 11, p. 352.
[8] *Inst. of Mech. Engs.*, 1910, p. 1663.

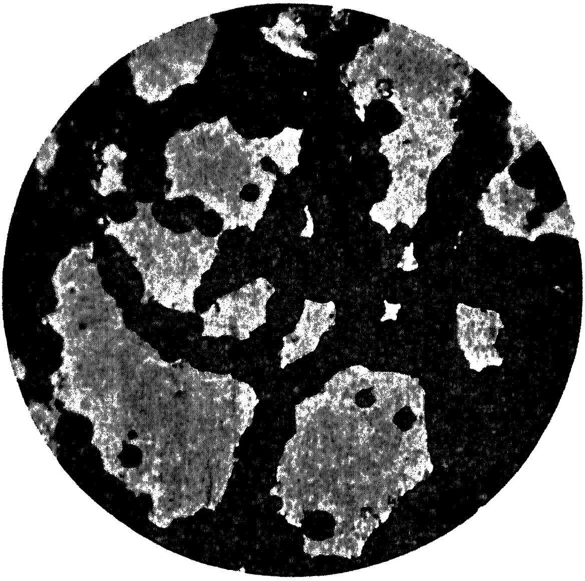


Fig. 76. Trootsite and Martensite. 250.

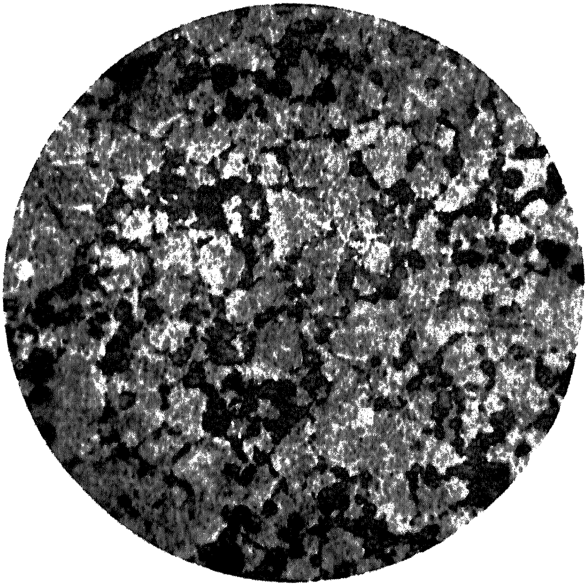


Fig. 77.—Trootsite and Martensite. Quenched Carbon Steel. × 150.

carbide of iron. M'Cance has conclusively proved that the permeability of quenched or tempered steels is greater as the amount of troostite they contain increases, which indicates that the iron contained therein is in the α and not the β-condition, as Benedicks suggested as a possibility. With this particular exception (β-iron), the two latest publications are in entire agreement, and since in the discussion on those two papers no facts were brought against these ideas, by investigators who had worked on the subject, many of whom took part in the discussion, it is safe to conclude that they embrace all the experimental facts that are at present known. The presence of troostite can be detected even during etching, because of its very quick etching rates, the areas in which it exists very quickly become black. When the two constituents, martensite and troostite, are present, the structure of the martensitic areas is only developed on prolonged etching (see fig. 78).

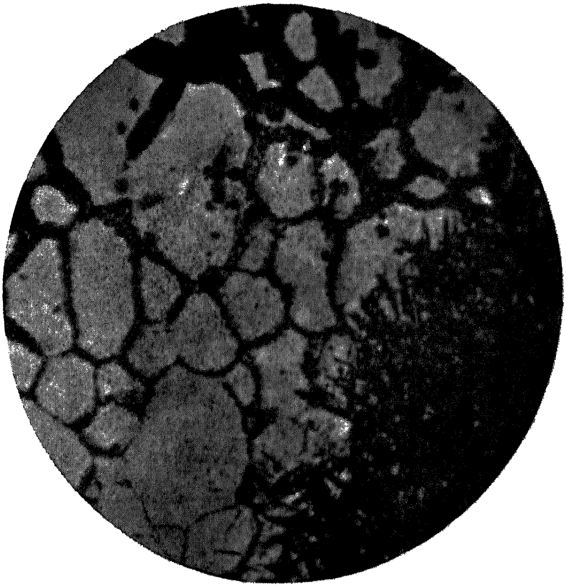


Fig. 78.—Quenched Carbon Steel. × 150.
Dark Areas = Troostite.
Light ,, = Unetched Martensite.

H. C. Boynton arranges the hardness of the various constituents that have been described as follows :—

TABLE II.

Constituent.	Relative Hardness.	Constituent.	Relative Hardness.
Ferrite, . . .	1	Austenite, . .	104·0
Pearlite, . . .	4·3	Martensite, . .	230·0
Sorbite, . . .	52·0	Cementite, . .	272·0
Trootsite, . . .	88·0		

CHAPTER VI.

THE SOLIDIFICATION OF STEEL INGOTS.

The changes that occur when steel passes from the liquid to the solid condition have been the subject of many laborious investigations, because they are, both from the scientific and practical standpoint, matters of very considerable interest. Watching an ingot of liquid steel solidifying at once suggests the two following questions:—What are the precise conditions which prevail throughout the mass? and what are the exact changes through which it is passing? These two questions are of great moment to the steel manufacturer, for it is upon their answer that the serious difficulties known as segregation, piping, blowholes, etc., have to be met.

As steel is a composite substance, its solidification from the liquid state involves more complications than are met with in the freezing of elementary or compound substances. There are, however, certain important phenomena that are more or less characteristic of all substances that crystallise when solidifying from the liquid state.

1st. Change in volume—*i.e.*, there may be a difference in the specific volume of the liquid and the solid crystals which are formed from it when just at the freezing temperature. This may either take the form of an increase or a decrease in volume during solidification.

2nd. When the mass is further cooled after complete solidification, the crystals progressively contract, unless, as is sometimes the case, they undergo an allotropic transformation or other internal change, which may involve an actual increase in volume at the particular inversion.

3rd. The solubility of gaseous impurities is almost invariably greater in the liquid than in the solid body, and in consequence a large proportion of the gas which may be held in liquid solution by the metal is suddenly liberated, whilst the solid crystals are being formed. Moreover, the solubility of gases in liquid metals varies considerably, and usually increases with the temperature. Hence, even whilst the liquid mass is cooling, and before any solid crystals have separated, relatively large volumes of gas are set free.

In addition to the above difficulties, each of which the steel metallurgist has to contend with, he is still confronted with another—viz., the fact that alloys like steel do not solidify bodily at one temperature, but over a range, which varies within wide limits according to the composition of the metal, and, as will be seen later, it is this circumstance which is the cause of the evil known as segregation.

Before discussing in detail the numerous defects to which ingot steel is subject, as a consequence of the above physico-chemical phenomena, a brief study of the freezing of less complicated substances will be advantageous.

We may first take the case of a perfectly pure liquid metal which is free even from traces of dissolved gases, but which contracts in volume when it passes from the liquid to the solid state. Under these conditions, when the liquid mass cools down to its solidifying temperature, crystals are deposited at the surfaces of the mould, and form a solid crust or shell around the liquid interior. These crystals take up positions approximately at right angles to the surfaces of the mould, and continue to grow inwards in that way as more solid separates from the liquid (see fig. 79). This process goes on until the whole mass has become quite solid by the freezing of the last trace of liquid in the central axis of the ingot. In perfectly pure metals or compounds the liquid which finally solidifies has exactly the same composition as that which was first formed at the outer shell of the ingot, and although at the later stages there is considerable difference between the temperature of the outside and centre of the ingot, the actual temperature at which each part passes from the liquid to the solid state is identical. The ingot is not, however, perfectly sound, because as each solid crystal is deposited it occupies a smaller volume than it did when in the liquid condition, and as the external dimensions of the ingot are decided in the early stages by the solid shell that is formed, this contraction in volume ultimately gives rise to a cavity or what is generally called "pipe" in the upper central axis of the ingot. In these

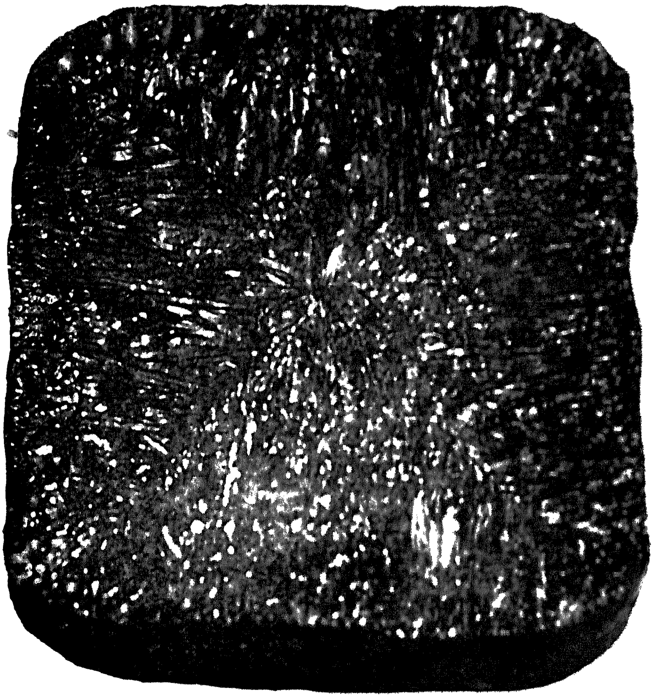


Fig. 79.—Broken Ingot, showing how the Crystals have grown from the Sides of Mould.

cases the surfaces of the pipe are generally smooth, and a vertical section of the ingot usually shows a cavity somewhat like that shown in fig. 80.

When there is no difference between the specific volume of the liquid and solid, little or no pipe is formed, and if an expansion occurs at the freezing temperature the top surface of the ingot will be more or less convex in shape.

With pure metals which in the liquid state take up gases either from the atmosphere or from the products of combustion that come in contact with them, the solid ingot is much less sound than in the above cases.

Although the solid metal may be capable of retaining a certain quantity of these gases in solution, its capacity in this respect is always less than that of the liquid, and in consequence a very large proportion, if not all, the gases held in solution by the liquid are liberated a little before or at the moment it passes into the solid state. Most of the gas which is set free in the early stages of solidification rise through the residual liquid interior and bubbles out at the top. Before long, however, this is prevented by the formation of a crust of metal at the top, which will not afford a free outlet for the gas which is subsequently liberated. Once this top crust has been formed, the gas still able to pass through the liquid finds its way into and goes to increase the size of the pipe which is forming in the ingot. There is usually a certain quantity of gas which does not reach the pipe, but is mechanically trapped inside the body of the ingot, owing to the metal becoming too viscous to allow it to rise. Some gas is also trapped by the branches of the skeleton crystals that are so rapidly thrown out, intercepting each other, and forming a solid boundary which encloses liquid. As this enclosed liquid solidifies, the gas which it throws out of solution is confined within the boundaries thus formed. The vertical section of an ingot which has solidified in this way will approximately present the appearance shown in fig. 81, with a pipe near the top and blowholes throughout the mass.

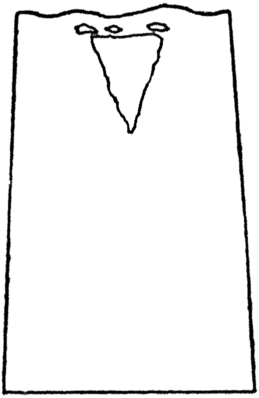


Fig. 80.

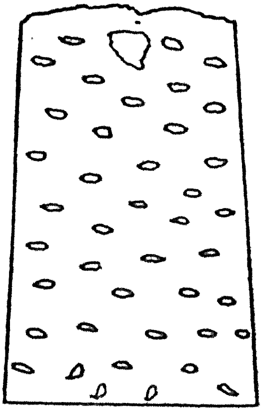


Fig 81.

In the cases hitherto considered, each part of the solid ingot has been assumed to possess the same chemical composition. With steel the conditions are totally different, because during the whole period of solidification the solid crystals that are being formed, and also the liquid, are constantly changing in relative composition. It is on account of this property that the percentages of carbon, sulphur, phosphorus, etc., which were uniformly distributed in the liquid metal, vary considerably in the solid ingot. The causes of this variation are of such a physico chemical nature as to make it both practically and theoretically impossible to produce large steel ingots which shall be absolutely uniform in composition. The liquid which is the last to solidify always contains a greater proportion of carbon, phosphorus, sulphur, etc., than the solid crystals which are formed during the early period of solidification. Since it is impossible to prevent this selective freezing, it follows that it is equally impossible completely to avoid segregation of the constituents of steel ingots, and the only thing which can be done commercially is to confine the evils of segregation within a reasonable limit.

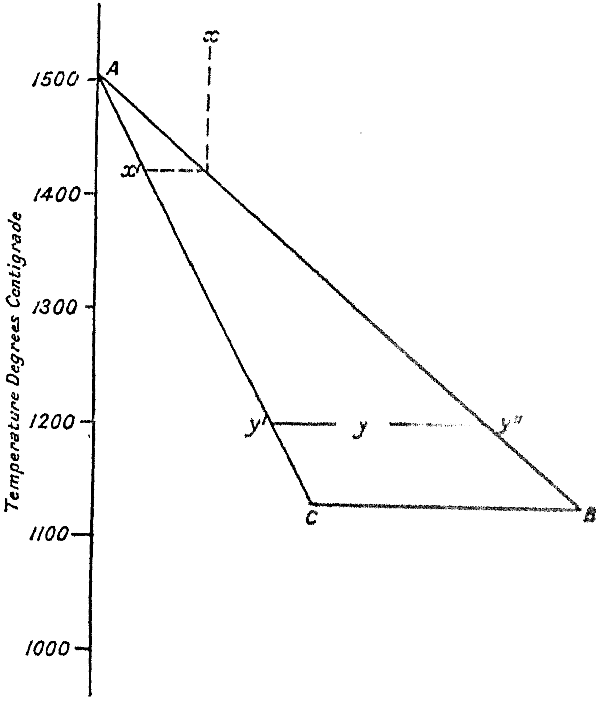


Fig. 82.

The manner in which segregation of carbon is brought about will be readily understood after a careful examination of fig. 82. The line A B represents the temperatures at which iron with varying percentages of carbon begins to solidify, and the lines A C B the temperatures at which the corresponding mixtures will just become solid if the rate of cooling be sufficiently slow to allow of perfect equilibrium being established between the liquid and solid at all temperatures within the freezing range. If the rate of cooling be quicker than is demanded for the theoretical equilibrium then the temperature at which the mass becomes completely solid is lowered, or, in other words, the last trace of liquid to solidify contains a higher percentage of carbon. At any temperature between the liquidus A B and solidus A C B the composition of the solid metal and of the liquid metal in equilibrium can be ascertained by drawing a line parallel to the base at the required temperature to meet the solidus and liquidus lines. The solid and liquid in equilibrium at temperature y are respectively represented by the points y' and y''. In the same way it will be seen that the composition of the last trace of liquid to solidify is represented by the point B. It is evident that the composition of the first crystals that are deposited from a liquid steel containing x per cent. of carbon (fig. 82) will contain x' per cent. of carbon, and the solid which subsequently settles around those primary crystal branches will contain more and more carbon as the temperature is lowered. If the rate of cooling be slow enough the excess of carbon contained in each of the successive layers of small crystals will diffuse inward to those that were previously formed, and which contain less carbon. The time that would be required for this diffusion to be complete is not known, but in the freezing of steel ingots under works conditions the cooling is certainly too quick to permit perfect diffusion. It is, therefore, impossible in commercial practice to prevent segregation. As the crystals grow towards each other and towards the centre of

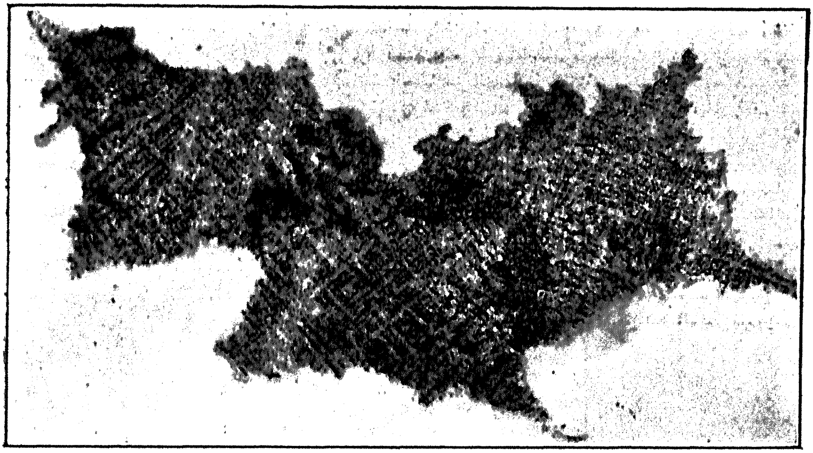


Fig 83 – Photo of an Auto Sulphur Print of the Section of Three Crystals of Steel (*Stead*).

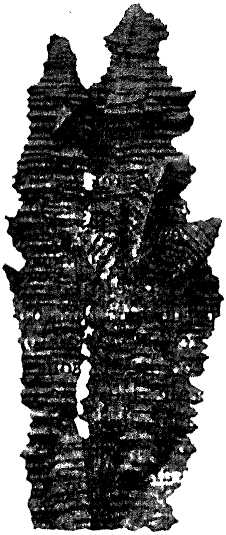


Fig. 84.—Group of Crystals taken from Pipe Cavity of Steel Ingot.

the mould, the remaining liquid which is constantly becoming richer in carbon is gradually driven into the centre of the ingot. Hence the outside shell of an ingot always contains less carbon than the average of the ingot; in fact, the carbon content increases with the distance from the surface upon which solidification began.

Both the sulphur and phosphorus contained in the initial liquid are concentrated in the final liquid to a greater extent than the carbon. This is largely due to the fact that they form mixtures with the iron, which have relatively much lower freezing points than the iron-carbon mixtures. Some of the segregation sulphur and phosphorus mixtures, like those of carbon, are mechanically trapped between the crystals which are formed at an early period, but a large proportion is progressively squeezed towards the centre of the ingot. The last trace of liquid which solidifies even around the crystals, and particularly towards the middle of the ingot, is, therefore, always relatively high in sulphur and phosphorus.

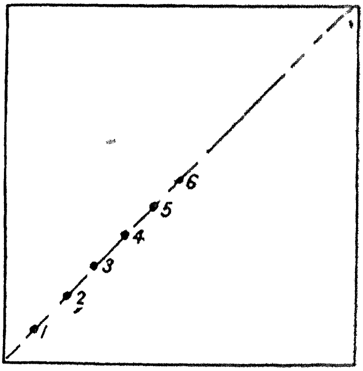


Fig. 85.

"Intercrystalline segregation" of sulphur is clearly shown in fig. 83, taken from a paper by Dr. Stead,[1] and the sulphide trapped in each crystal serves to show its dentritic structure. Fig. 84 is a photograph of a bunch of crystals taken from the pipe cavity of a steel ingot.

Segregation.—Mr. Stubbs[2] was probably the first to draw attention to the fact that cast-steel ingots are not chemically homogeneous, and that a redistribution of the elements, carbon, sulphur, and phosphorus, takes place during solidification. G. J. Snelus[3] confirmed this, and gave analyses obtained from a large ingot 7 feet long and 19 × 19 inches. Two slices of this ingot were cut off, one 21 inches from the top and the other 4 inches from the bottom. Drillings were taken from each slice along a diagonal line, and numbered as shown in sketch (fig. 85).

[1] *Cleveland Institute of Engineers*, 1912.

[2] *Iron and Steel Inst.*, No. 1, 1881, p. 200.

[3] *Ibid.*, No. 2, 1881, p. 379.

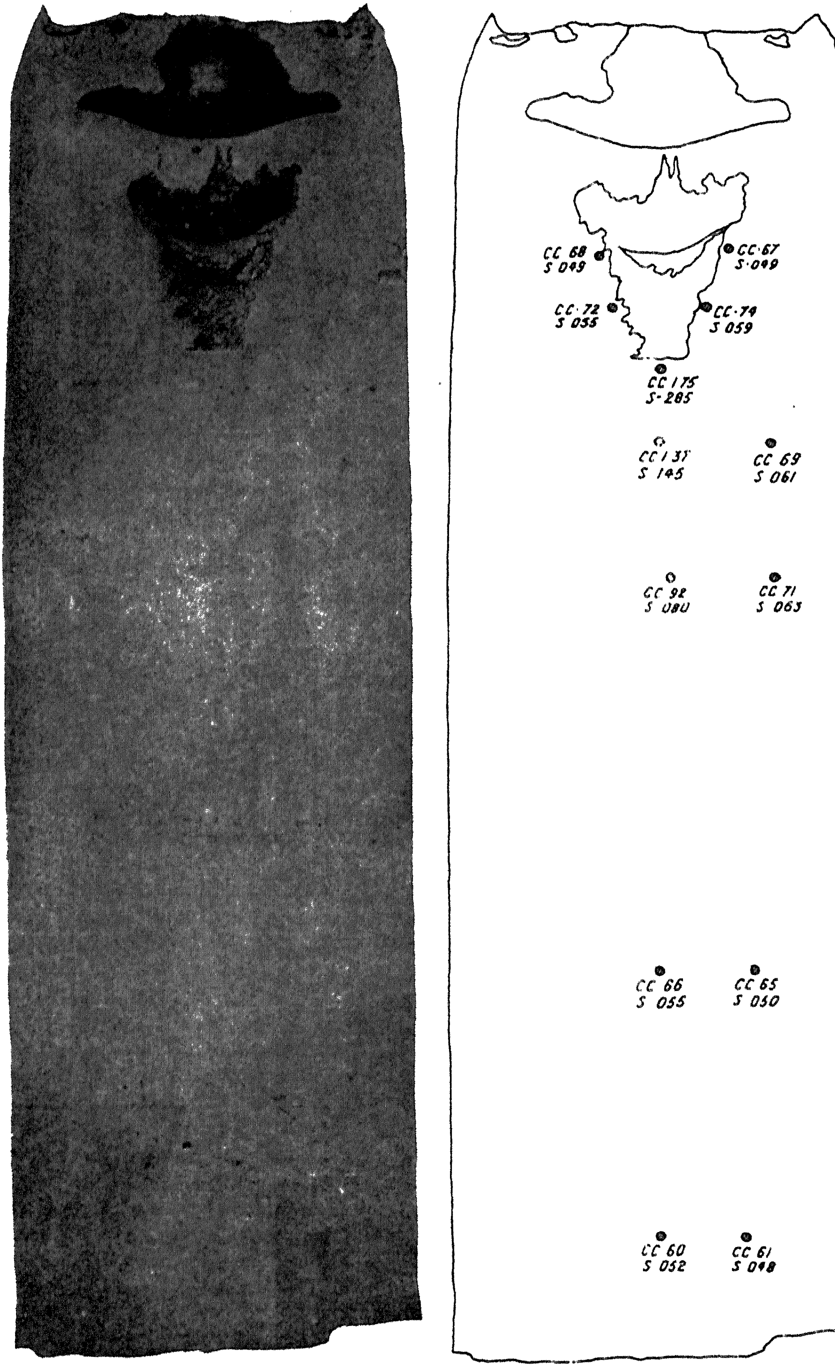


Fig. 86.—Ingot cut through Centre (*Talbot*).

The analyses of these drillings were as follows :

	Top.			Bottom.		
	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.
1	·44	·032	·044	·44	·048	·060
2	·54	·048	·060	·42	·056	·062
3	·57	·080	·086	·41	·048	·054
4	·61	·096	·097	·40	·048	·054
5	·68	·120	·111	·38	·048	·058
6	·77	·180	·142	·37	·044	·052

As regards the top section, it will be seen that the percentages of each of the three elements increase on passing from the outside to the centre of the ingot. In the bottom section, however, whilst there is a slight irregularity, there is a tendency for the carbon, silicon, and phosphorus contents to become less on passing from the outside to the centre. Both these effects are due to the drillings having been taken very close to the bottom of the ingot.

Some idea of the distribution of carbon, phosphorus, and sulphur in steel ingots may be obtained by referring to the analyses given in fig. 86.

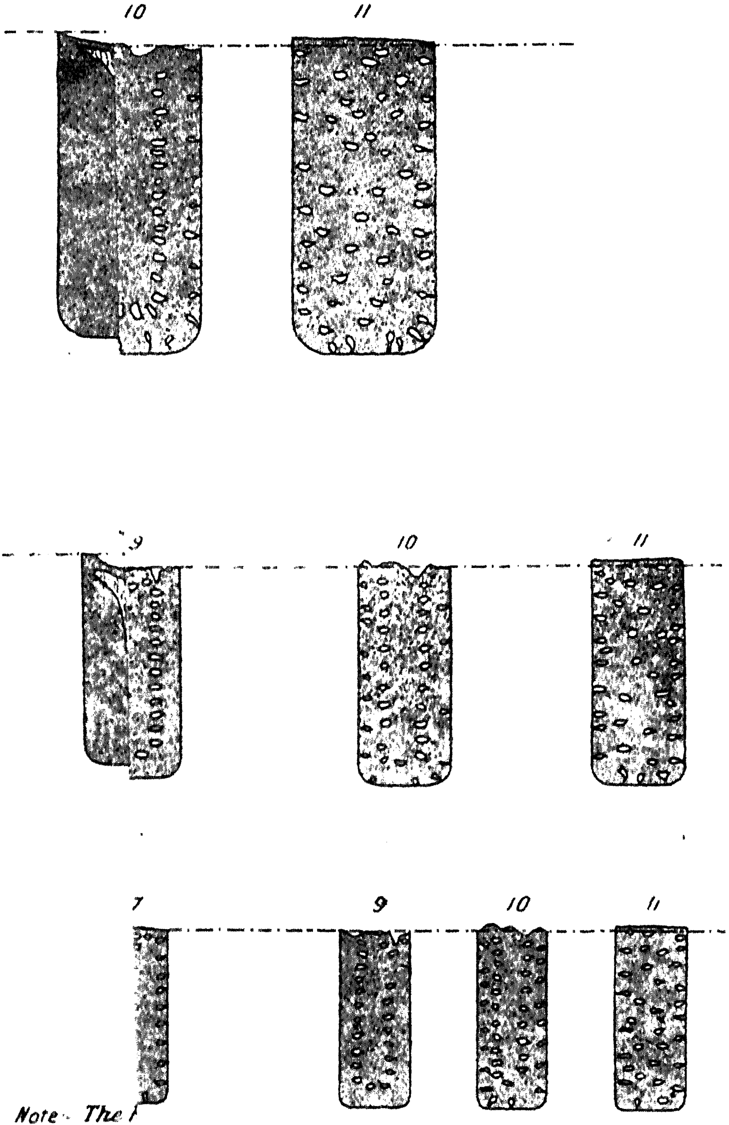
The Position of the Pipe and of the Blowholes in Steel Ingots.

Amongst the earliest investigators of the occurrence of blowholes in steel ingots was C. A. Caspersson.[1] The main feature of his work lies in what is called the "Caspersson table," which deals with the quality of the ingots in relation to the casting temperature and carbon content. There is no doubt that the temperature to which steel is subjected during the final stages of its manufacture has a marked effect upon the quantity of such gases as hydrogen, nitrogen, oxides of carbon, etc., it will take up and hold in solution. The extent to which the metal will dissolve these gases increases with rising temperature and with decreasing carbon content. It has, however, been conclusively demonstrated by Brinell's work, communicated by Wahlberg,[2] that, apart from carbon, the chemical composition is an all-important factor in determining the capacity of the metal for dissolving gases. The presence of silicon, manganese, and aluminium materially increases; for example, the amount of gas which can be retained in solution. The occlusion of gases by steel is not permanent, for when the metal is cast and the temperature falls, a point is reached at which they begin to be liberated from solution. This evolution continues with further cooling, and whilst part of the gases completely escapes from the liquid mass and thus becomes harmless, some remains in the ingot and forms the cavities known as "blowholes." The extent to which these blowholes are formed, and also

---

[1] Jernkontoret's Annaler, 1882, 5. *Iron and Steel Inst.*, 1883, No. 1, p. 480.

[2] *Journ. Iron and Steel Inst.*, No. 1, 1902.



Note.- The
indic
withi
after

Types.

their position in an ingot, depends very largely upon the particular stage at which the gases are thrown out of solution—*i.e.*, whether before or after the solidification of the top surface of the ingot. Under normal conditions Brinell says that the factors which determine the soundness of steel ingots are those which hasten or retard the evolution of the gases occluded in the liquid metal. The increased tendency of the gases to become disengaged as the cooling proceeds is counteracted by the presence of aluminium, manganese, and silicon, and if sufficient of these elements be present, the steel will become quite solid without any appreciable quantity of gas being liberated. As the quantity of aluminium + silicon + manganese present falls below a certain limit, the temperature at which the gases are set free is raised above that at which the mass solidifies. In fact, steel which contains practically none of the above elements begins to liberate the gases from solution almost as soon as it enters the mould, and the top surface of the metal is

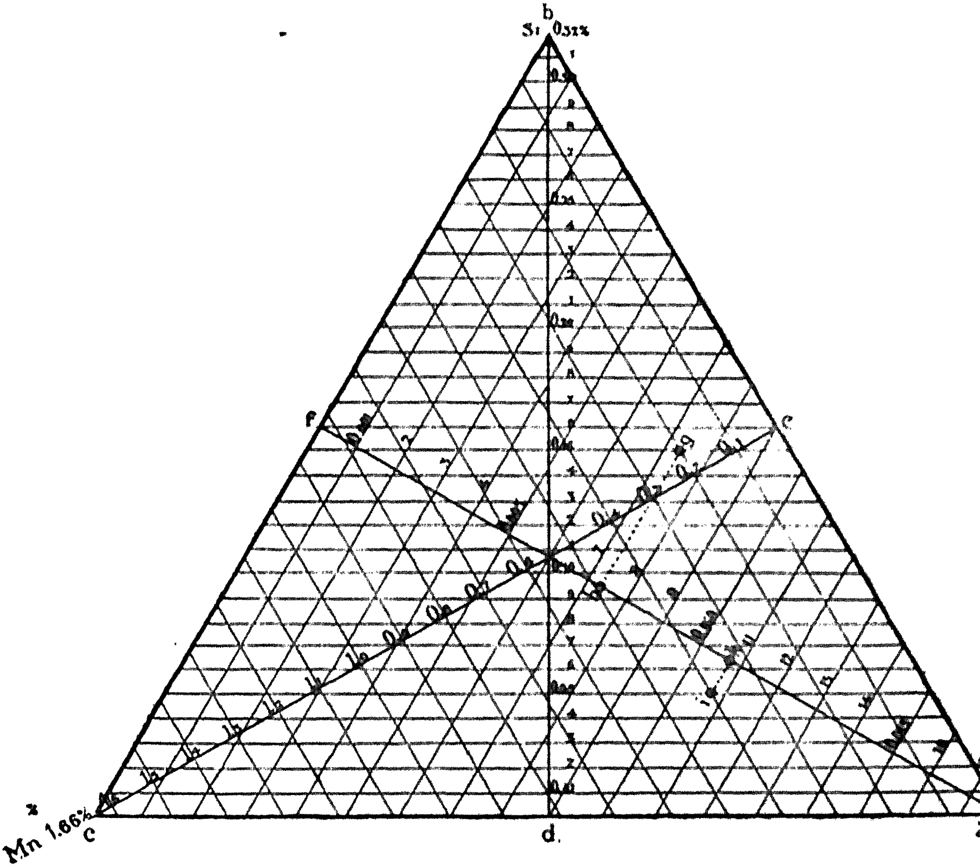


Fig. 95.

kept in constant agitation by the bubbles of gas rising from the mass. If there be too much aluminium, silicon, or manganese present, the steel is technically termed "killed," which means that no gas is set free during solidification. In such circumstances no blowholes are formed, but the piping cavity is both larger and deeper. The size of the ingot exerts an influence upon the position of blowholes, inasmuch as it affects the rate of solidification. Vertical sections of Brinell's standard types of ingot are shown in fig. 87, and some of the corresponding transverse sections in figs. 88 to 94. Each vertical series represents ingots containing the same corrected and combined percentages of aluminium, silicon, and manganese. This arrangement of the ingots affords a very good conception of the effect of size upon the soundness of ingots. Thus, it will be seen that, as the size of the ingot decreases, less aluminium, silicon, or manganese is required to produce the soundest type of ingot (No. 5). From his many researches Brinell determined the relative effect of the above-mentioned elements upon the soundness of steel ingots. He concludes that aluminium has 90 times as much effect as manganese and 17·3 times as much as silicon. Thus, 1·66 per cent. of manganese without any silicon or aluminium, 0·32 per cent. of silicon without manganese or aluminium, and 0·0184 per cent. of aluminium without manganese or silicon, will give the same type of ingot as regards the position of the blowholes, etc. From these figures Brinell constructed a triaxial diagram (fig. 95) by means of which the percentage of aluminium or silicon to add in order to produce the No. 5 type of ingot for any given manganese content can be readily determined. Thus, a steel containing 0·40 per cent. of manganese and 0·12 of silicon will require the addition of 0·0068 per cent. of aluminium. It should be remembered that, whilst Brinell's ratios as given above are probably independent of the size of ingot, the actual quantities relate only to ingots 10 inches square, and to metal top cast into almost cold moulds with walls 2 inches thick. If these conditions be varied, the amount of aluminium, etc., it is necessary to add in order to produce the desired effect also varies. This is clearly indicated by the illustrations given in fig. 87.

Blowhole Segregation.

The interesting and important practical fact that the blowholes formed in steel ingots during solidification may constitute pockets in which liquid segregates, containing high percentages of impurities, can subsequently collect was first demonstrated by Dr. Stead.[1] He examined an ingot which had the following dimensions and analysis:—

Dimensions—	
Length, ...	5 feet 2 inches.
Breadth, ...	2 ,, 2 ,,
Thickness, ...	1 ,, 8 ,,
Analysis—	
Carbon, ...	0·13 per cent.
Manganese, ...	0·32 ,,
Sulphur, ...	0·064 ,,
Phosphorus, ...	0·034 ,,

---

[1] "When Steel Freezes," *Cleveland Institute of Engineers*, 1912, p. 33.

He says:—"There was evidence that the steel had risen in the mould after casting to the extent of about 6 inches—a clear indication of unsoundness or honeycombing. The fracture showed an outer solid layer of about ¾ inch; then honeycombs for about 2½ inches, tapering inwards, but very unevenly; then perfectly sound steel to the centre. It resembled Brinell's type Nos. 6 and 7, excepting that the envelope of solid steel was thicker, and that many of the blowholes, instead of being so continuous, about half of them were continued to the full distance of 2½ inches. In one place, at a distance of ½ inch from the outside, there were about thirty small cavities per square inch, the mean diameters being respectively about $\frac{3}{64}$ inch and $\frac{3}{16}$ inch. Some of the blowhole walls were tinted brown and yellow, and many were coated at their inner extremities with a dull grey layer. On placing slips of acidulated bromide paper against these dark films, the films readily dissolved, leaving bright metallic surfaces of steel below, whilst the silver bromide was blackened by the evolution of hydric sulphide—a proof that the films were rich in sulphides. It was noticed that beyond the termination of the large continuous radial blowholes there were a few isolated independent spherical cavities. As it seemed probable that these might be associated with blowhole segregations, sections were cut from the steel where they were detected. Examination of one of these proved that there was segregation. The photograph (fig. 96) shows the position of one of the cavities and the accompanying segregate. This indicates that the hole was originally twice the size of the remaining cavity, and that about half of its volume is occupied by a segregate rich in phosphorus and sulphur, which had been forced into it by internal pressure." Dr. Stead estimated that the segregate contained at least 0·40 per cent. of sulphur and 0·50 per cent. of phosphorus. He considers that at the high temperatures of solidification the sulphur is in combination with iron as FeS, and not with the manganese. This view is strongly supported by the

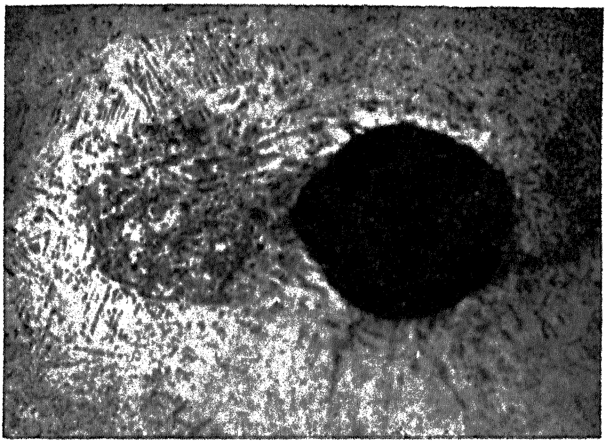


Fig. 96.—Blowhole Segregation showing Remains of Original Blowhole and the Segregate which had been forced into the Cavity (*Stead*).

fact that, whilst the segregation of sulphur is quite marked, that of manganese is almost negligible. At lower temperatures sulphide of manganese is formed in accordance with the following reaction :—

$$FeS + Mn = Fe + MnS.$$

The fact that blowhole segregation of sulphur will occur in a steel ingot with a normal average percentage of sulphur is very important to the steel manufacturer, because if the blowholes happen to be situated comparatively near the outer surface of the ingot (see types 6 and 7, figs. 87 and 91), they will involve a marked concentration of sulphur where it is least desired. This kind of sulphur segregation in what may be otherwise regarded as good steel, will undoubtedly produce red-shortness and surface cracking during the rolling of the material. A steel of excellent average composition may thus give all the characteristic features of high sulphur steel, which means greater trouble in the rolling mill and a poorer surface finish on the final article.

As showing the extent to which blowhole segregation may develop, another example may advantageously be considered. This was a case of a rather heavy steel casting, which had to be machined. The average phosphorus content was somewhat abnormal—viz., 0·14 per cent. When placed in the lathe for machining it was found that the tool had no effect whatever upon one side of a flange marked A, fig. 97, whilst no difficulty was experienced in machining any other part of the casting. On breaking pieces off that part of the casting large numbers of blowholes were found immediately underneath the skin. The broken pieces were quite brittle, and an analysis showed that the average phosphorus content was over 0·6 per cent. A microscopic examination clearly demonstrated that in certain areas the phosphorus was even as high or higher than 10·0 per cent. (see photograph, fig. 98).

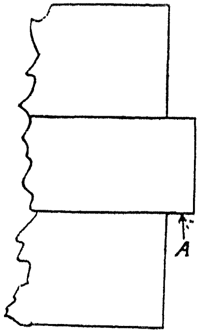


Fig. 97.

Blowhole segregation is caused by the high gaseous pressures inside the ingot forcing the impure liquid into the previously formed cavities. In the early stages of solidification the liberated gases can escape freely from the top surface of the ingot, but when the top is sealed the gases accumulate and exert very high pressures inside the ingot.

There have been many papers published dealing with the effects of piping and segregation, and the means by which these evils can be minimised and, under certain conditions, more or less neutralised. It is not possible in a work of this nature to give a complete bibliography of the subject, but this has recently been so ably done by Sir Robert Hadfield[1] as to render it unnecessary now. In a paper by H. M. Howe,[2] in which he deals with the causes and prevention of piping in steel ingots, and the causes and restraint of segregation, he arrives at the following conclusions :—

[1] "Method of Producing Sound Ingots," *Iron and Steel Inst.*, No. 2. 1912, p. 111.

[2] *Bi-Monthly Bulletin of the American Institute of Mining Engineers*. 1907, pp. 169-274.

The pipe is shortened and the position of the segregate in the ingot is raised—

(1) By top-casting instead of bottom-casting;
(2) By slow casting;
(3) By casting with the large end up instead of down;
(4) By retarding the cooling of the top by means of a sinking-head or otherwise;
(5) By liquid compression; and
(6) By permitting deep-seated blowholes to form through adjusting the quantity of silicon and manganese or their equivalents.

The pipe is shortened and segregation probably increased—

(7) By casting in wide ingots;
(8) By using moulds of low conducting power—*i.e.,* lined with sand or clay;
(9) By using pre-heated moulds.

Segregation is restrained—

(10) By casting as cool as practicable; and
(11) By casting in small ingots.

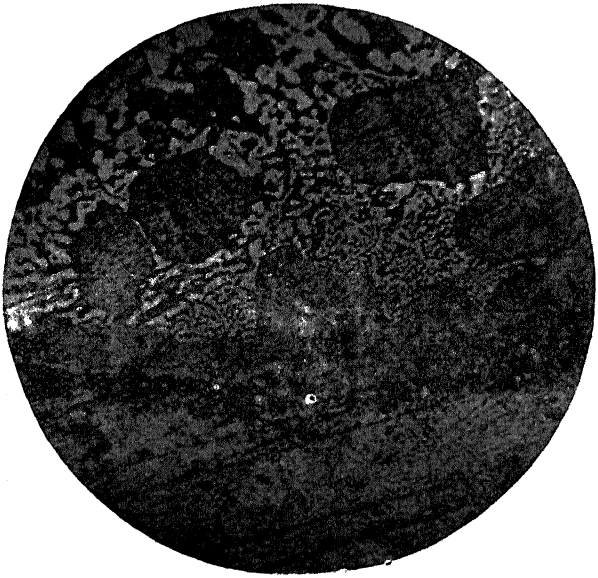


Fig. 98.—Blowhole Segregation of Phosphorus in Cast Steel.

Fluid Compression.

Broadly speaking, there are four methods in use for subjecting steel ingots to high pressures, whilst the interior is still in the liquid condition. These are the Whitworth, Illingworth, Harmet, and Williams processes. In each of these the object aimed at is to counteract the natural tendency to form a piping cavity as a result of internal contraction by reducing the

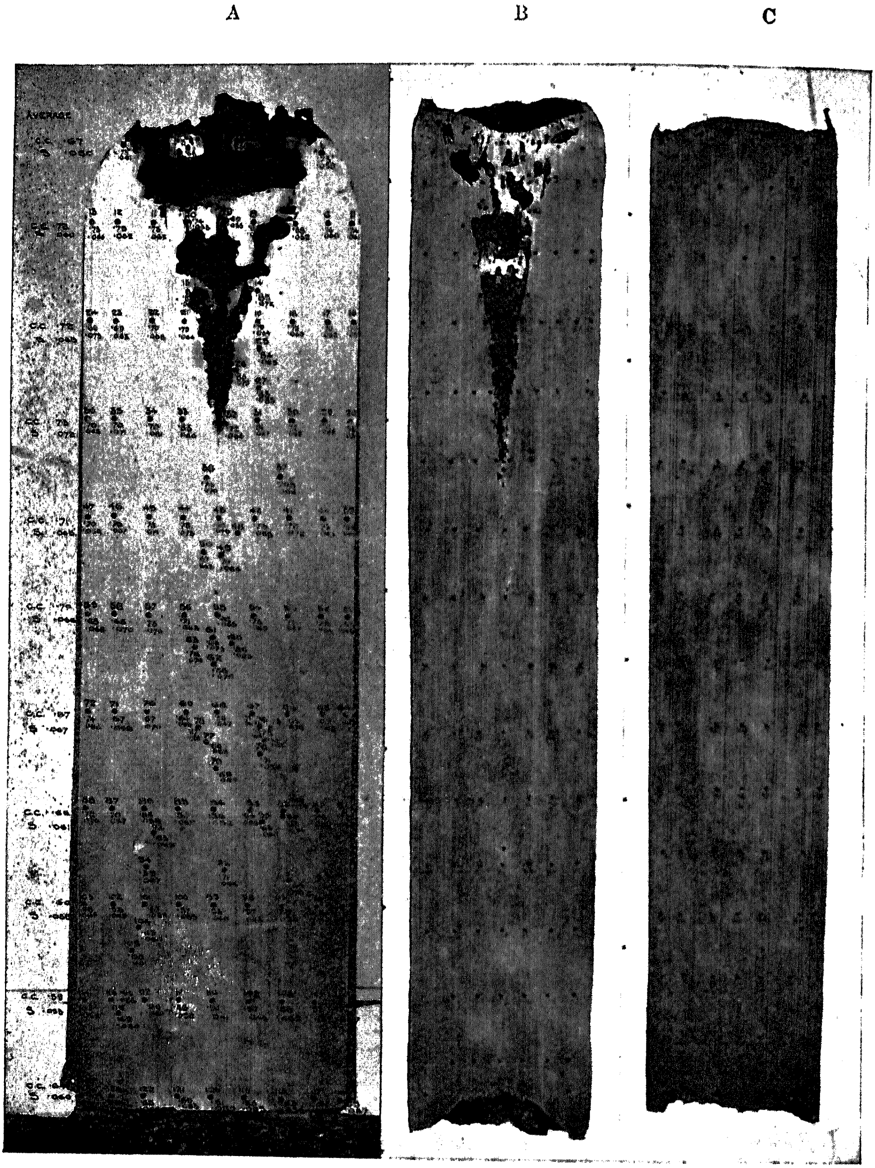


Fig. 99.—No. 3 Series. Steel with Aluminium Additions (*Talbot*).

A.—Ingot cut down longitudinally through the centre, showing cavity.

B.—Semi-cogged ingot, cut down longitudinally through the centre, cogged as in ordinary practice, showing the cavity not filled up at this stage (20 × 25-inch ingot cogged down to 18 × 18 inches).

C.—Semi-cogged ingot, cut down longitudinally through the centre, cogged whilst centre still fluid, showing cavity to have disappeared at this stage (20 × 25-inch ingot cogged down to 18 × 18 inches).

external dimensions of the ingot. Liquid compression also minimises the degree of segregation. The above-mentioned methods differ in the manner of applying the pressure. Briefly, the pressure is applied lengthways in

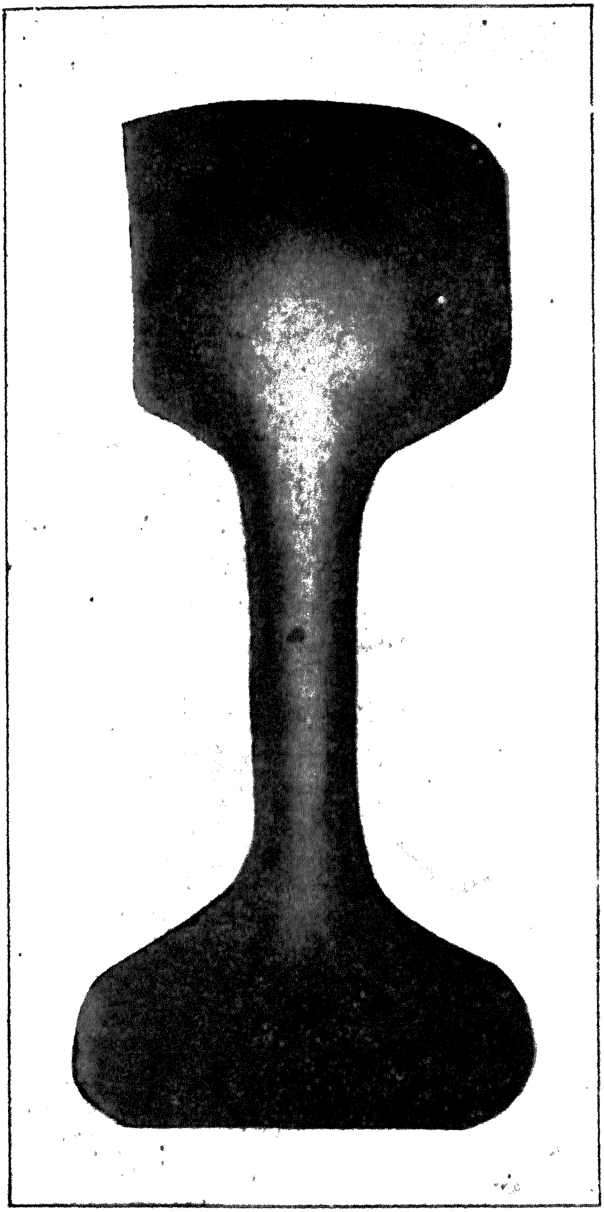


Fig. 100.—Rail treated by Talbot Process.

Whitworth's process, in Illingworth's process sideways and uniformly, in Harmet's process endways in a conical mould, and in Williams' process sideways and chiefly near the middle of the ingot.

Quite recently Talbot[1] has introduced a new method, which apparently possesses the advantages of being relatively simple and inexpensive. In this method lateral compression is applied by cogging the ingot down, in the ordinary cogging mill, whilst the centre is still liquid. The inventor of this process suggests that it may be applied to such classes of steels as rails, etc. It is, however, admitted that to do this a much better control over the times of tapping the furnaces would have to be secured, and an extremely careful regulation of the times, between casting and cogging down would have to be maintained.

The complete removal of the piping by Talbot's method of lateral compression is very clearly illustrated in fig. 99. The longitudinal section through the centre of an ingot which has been allowed to solidify in a normal manner is shown in A, and from which the position and size of the pipe cavity can be seen. B is a section of a similar ingot which has been partly cogged down, and as the whole of the ingot was solid, the cogging has simply elongated the cavity. C represents the vertical section cut through the centre of another ingot of the same kind, but which was put through the cogging mill whilst the interior was still liquid.

Another interesting fact concerning this process is that it actually displaces the segregate from its normal position in the upper central part of the ingot, and distributes it fairly evenly between the outer vertical walls and the central axis of the ingot. Hence rails, etc., manufactured from ingots that have been treated in this way do not contain the segregated area in the middle parts of the section, but in the positions shown in fig. 100.

---

[1] *Iron and Steel Inst.*, 1913, No. 1, p. 30.

CHAPTER VII.

IRON-CARBON STEELS.

THE effect of carbon on the mechanical properties of steel has been the subject of many investigations, notably by Prof. Arnold[1] amongst others. The analyses of the steels with which he experimented are given in Table III. From these figures it will be seen that the percentages of all the impurities, including manganese, are extremely low, and, therefore, the mechanical properties of the series may be accepted as being representative of pure iron-carbon steels. It is, however, necessary to note that in the annealed samples the two steels containing 1·20 and 1·47 per cent. of carbon there was respectively 0·28 and 1·14 per cent. of carbon in the uncombined or graphitic condition. This is an interesting fact, because it very forcibly illustrates the facility with which carbide of iron, Fe_3C, is decomposed into its constituents when the steels are practically pure iron-carbon alloys. It also shows the necessity of having a certain quantity of manganese in high carbon steels to retard or prevent this decomposition.

The figures for the tensile properties of the series in the annealed state are given in Table V., and plotted graphically in figs. 101 and 102. In this instance the term annealing refers to heating the bars in quicklime in a covered cast-iron box to a temperature of 1,000° C. for 72 hours, and then allowing them to cool in the luted furnace during 100 hours.

TABLE III. ANALYSES.

Total Carbon.	G. Carbon in Annealed Steels.	Silicon.	Manganese.	Phosphorus.	Sulphur	Aluminium.
0·08	..	0·03	0·02	0·02	0·03	0·02
0·21	..	0·05	0·05	0·02	0·03	0·02
0·38	.	0·03	0·08	0·02	0·02	0·03
0·59	..	0·07	0·10	0·02	0·02	0·03
0·74	..	0·05	0·01	0·02	0·02	0·02
0·89	..	0·03	0·09	0·02	0·02	0·03
1·20	0·28	0·07	0·15	0·02	0·02	0·03

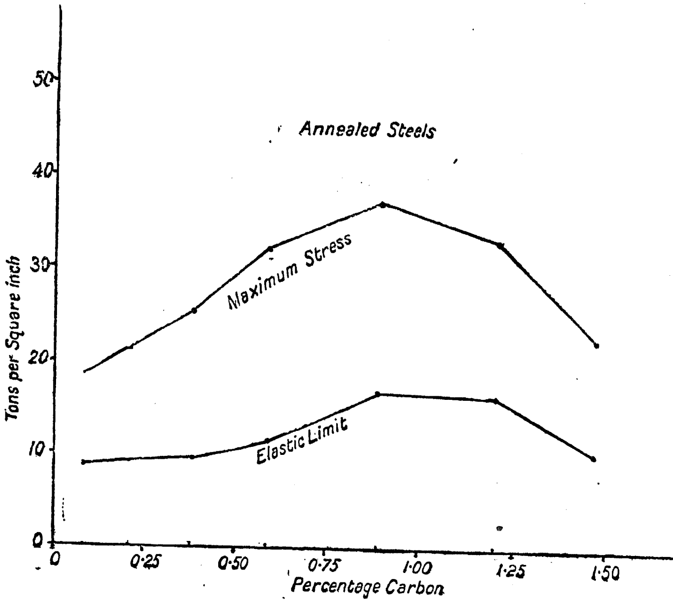


Fig 101.—(*Arnold*).

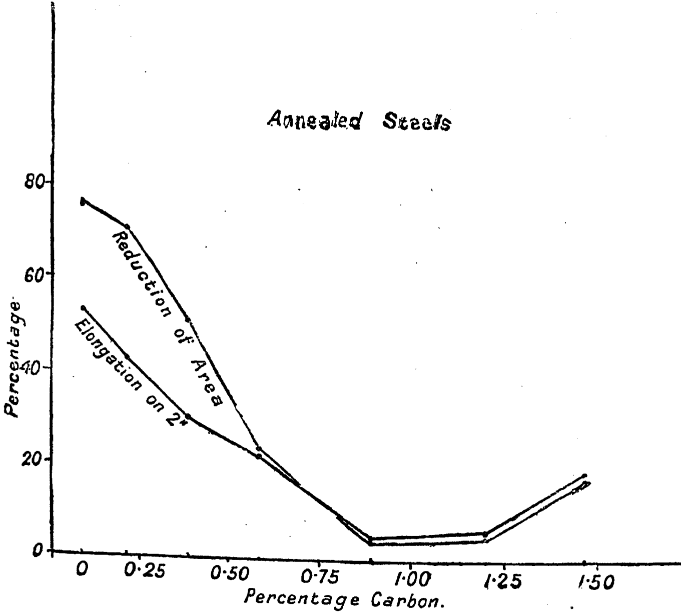


Fig. 102.—(*Arnold*).

TABLE IV.—TENSILE PROPERTIES OF ROLLED BARS.

Carbon.	Elastic Limit.	Maximum Stress.	Elongation on 2".	Reduction of Area.
	Tons per sq. in	Tons per sq. inch.	Per cent.	Per cent.
0·08	12·19	21·39	46·6	74·8
0·21	17·08	25·39	42·1	67·8
0·38	17·95	29·94	34·5	56·3
0·59	19·82	42·82	19·9	22·7
0·89	24·80	52·40	13·0	15·4
1·20	35·72	61·65	8·0	7·8
1·47	32·27	55·71	2·8	3·3

It will be observed that the elastic limit and ultimate stress progressively increase with the carbon up to 0·89 per cent., and then decrease as the carbon is further raised. The ductility of the same specimens, as represented by the elongation and reduction of area, falls as the carbon is raised to 0·89 per cent., and then again increases. This increased ductility is really due to the presence of free ferrite resulting from the decomposition of carbide of iron. The discontinuity in the properties which occurs with 0·89 per cent. of carbon in annealed steels is, however, evident, even when the whole of the carbon is in the combined state. It is explained by the fact that at 0·89 per cent. of carbon the steel corresponds with the eutectoid composition. With less

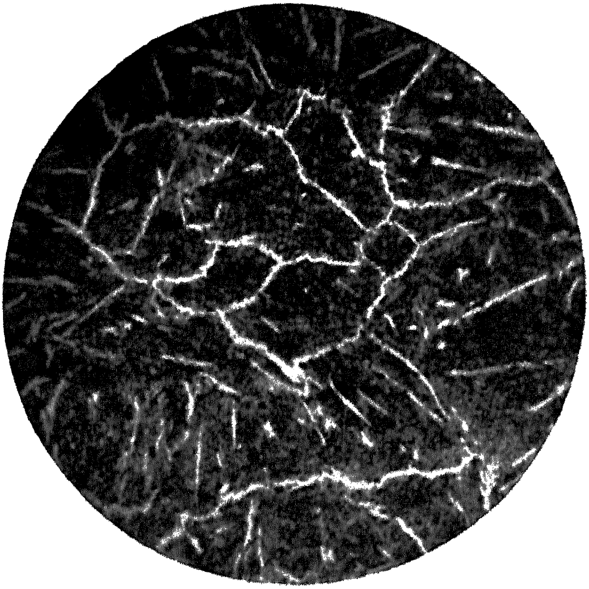


Fig. 103.—Carbon Steel.

Carbon = 1·20 per cent.
White = Cementite.
Dark = Pearlite.

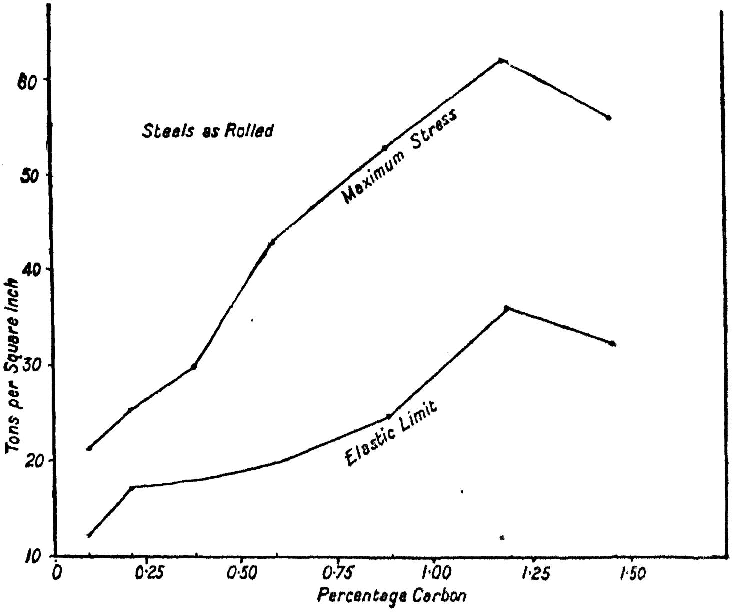


Fig 104.—(*Arnold*)

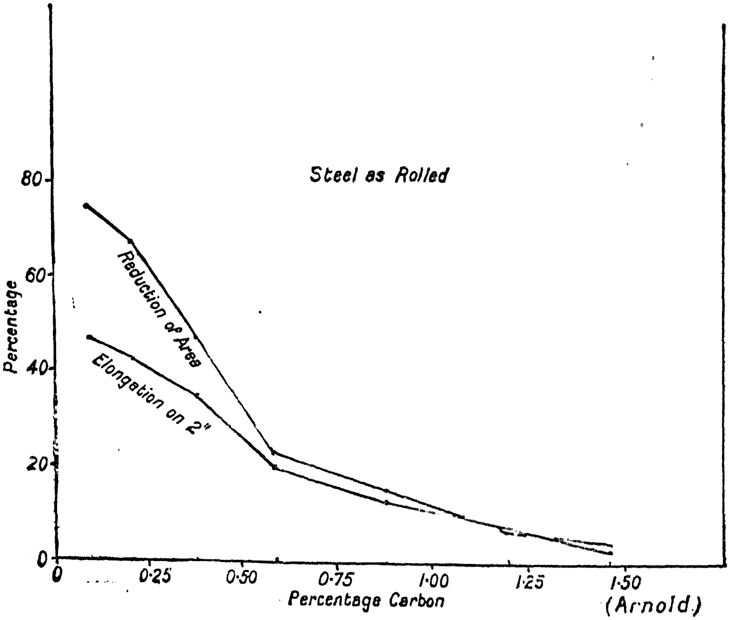


Fig. 105.

than that amount of carbon there exists an excess of ferrite over that requi to form the mixed constituent known as pearlite. With more carbon f cementite or carbide of iron surrounds the pearlite (see fig. 103), and the ha brittle nature of cementite in this form brings about a deterioration in mechanical properties of the mass.

The properties of the same steels in the unannealed or rolled condit are given in Table V., and plotted in figs. 104 and 105. As would be expect it will be seen that the elastic limit and ultimate stress are higher than the annealed specimens, whilst the elongation and reduction of area lower. The abrupt change in the tensile properties does not occur at eutectoid composition, but at 1·25 per cent. of carbon. This is, no dou due to the cellular walls of cementite having been broken up in the operat of rolling, an action which apparently is not possible when the carbon reac 1·47 per cent.

TABLE V.—TENSILE PROPERTIES OF ANNEALED BARS.

Carbon.	Elastic Limit.	Maximum Stress.	Elongation on 2″.	Reduction of Ar
	Tons per sq. in.	Tons per sq. inch.	Per cent.	Per cent.
0·08	8·82	18·34	52·7	76·7
0·21	9·02	21·25	42·3	65·7
0·38	9·55	25·02	35·0	50·6
0·59	11·36	31·87	22·0	23·3
0·89	16·81	36·69	4·5	4·2
1·20	16·19	32·87	6·0	4·9
1·47	10·08	22·33	19·0	17·7

From the above figures it will be seen that the mechanical propert of steel are very materially influenced by the mechanical or heat-treatm to which they are subjected. Variations of this kind are invariably acco panied by more or less well-defined differences in the structural constituti of the mass. Most of these structural differences are readily revealed by examination under the microscope, and an approximate idea of the propert of the steel may thus be obtained. Broadly speaking, any treatment wh reduces the size of the constituent crystals contained in a metallic all such as steel, brings about an increase in the elastic limit and ultimate stre and a corresponding fall in the ductility, and *vice versâ*. Various hypothe have been advanced to explain this, but at this stage it is unnecessary refer to them.

A very clear illustration of the influence of crystal size upon the p perties of steel is shown in fig. 106, which depicts four well-defined conditi in which the pearlitic areas may exist in steel, and their correspondi mechanical properties. It is, therefore, quite obvious that a chemical analy alone is no real guide in deciding the mechanical properties of steel. T factors which affect the internal structure, and consequently the propert of steel, are :—

1st. The temperature to which it is heated prior to rolling, and the ti it is kept at that temperature.

2nd. The amount of deformation, or reduction of area, during rolling.

3rd. The finishing temperature of rolling.
4th. The rate of cooling.

In regard to the first, the crystals of steel grow when at temperatures above the highest recalescence point, and the rate of this growth increases as the temperature is further raised. The time factor is also an important item in this connection, and this is especially the case at very high temperatures.

2nd. During rolling, the deformation of the metal is constantly breaking up the crystals into smaller ones.

3rd. Since the recrystallisation and crystal growth which is proceeding during the process of rolling is retarded as the temperature falls, it follows that the lower the finishing temperature the smaller will be the crystals in the finished steel.

4th. The rate of cooling plays a very important rôle, and this is more particularly so as regards the range of temperatures between about 700° C. and 500° C. It is within these temperatures that the troostitic pearlite, which is first formed as the steel cools through the Ar_1 change, passes into the coarser forms of the same constituent.

From the foregoing, it will be recognised that any formula for calculating the strength of steel from its chemical composition can have only a limited application, and to be of any real value the conditions of manufacture must be known, and should be the same as those which prevailed for the standards from which the formula was deduced.

H. H. Campbell[1] has made a most careful study of this subject, and from a very large number of observations he has established a number of formulæ. The results upon which he bases his conclusions were obtained from steel bars 2 inches by ⅜ inch, which had been hammered and rolled from ingots 6 inches square. Campbell's conclusions are as follows :

Carbon.—In acid steel each 0·01 per cent. of carbon strengthens steel by 1,000 lbs. per square inch, when the carbon is determined by combustion. The strengthening effect is 1,140 lbs. for each 0·01 per cent., as determined by colour, owing to the fact that the colour test does not determine all the carbon present.

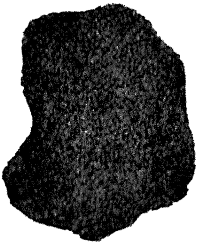
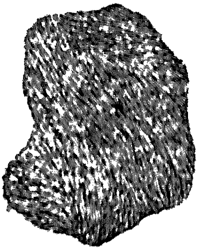
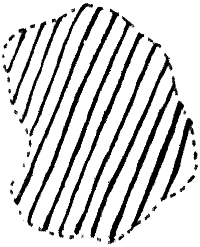
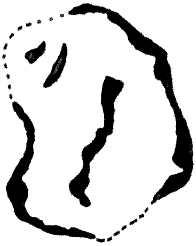
In basic steel each 0·01 per cent. of carbon strengthens steel by 770 lbs. per square inch when the carbon is determined by combustion. The strengthening effect is 820 lbs. for each 0·01 per cent., as determined by colour.

Phosphorus.—Each 0·01 per cent. of phosphorus strengthens steel by 1,000 lbs. per square inch.

Manganese.—Each 0·01 per cent. of manganese has a strengthening effect upon steel, and the effect is greater as the carbon content increases. Below a certain content of manganese the effect is complicated by some disturbing condition, probably iron oxide, so that a decrease in manganese in very low carbon steels is accompanied by an increase in strength. In acid steel each increase of 0·01 per cent. of manganese above 0·4 per cent. raises the strength of the steel an amount varying from 80 lbs. in a metal containing 0·1 per cent. carbon to 400 lbs. in a metal containing 0·40 per cent. of carbon. In basic steel each increase above 0·3 per

---

[1] *Journ. Iron and Steel Inst.*, No. 11, 1904, p. 61.

Mechanical Properties of Mass.	Microstructure.	Segregation Stages.
Maximum tensile stress about 70 tons per square inch. Elongation on 2 inches = about 10 per cent.		1ST PHASE. "Sorbitic" pearlite with emulsified Fe_3C. Very dark on etching.
Maximum tensile stress about 55 tons per square inch. Elongation on 2 inches = about 15 per cent.		2ND PHASE. Normal pearlite with semi-segregated Fe_3C. Dark on etching.
Maximum tensile stress about 35 tons per square inch. Elongation on 2 inches = about 5 per cent.		3RD PHASE. Laminated pearlite with completely segregated Fe_3C. Exhibiting a play of gorgeous colours when lightly etched.
Maximum tensile stress about 30 tons per square inch.		4TH PHASE. Laminated pearlite passing into massive Fe_3C and ferrite.

Note.—It is important to remember that in a single section of steel two or even all three phases of pearlite may be observed in juxtaposition gradually merging into each other.

Fig. 106.—Showing the Properties of Pearlite and its Decomposition Product. Fe_3C represented Black (*Arnold* and *M'William*).

cent. raises the strength an amount varying from 130 lbs. in a metal containing 0·1 per cent. of carbon to 250 lbs. in a metal containing 0·4 per cent. of carbon.

Sulphur.—The effect of sulphur on the strength of acid and of basic steel is very small.

Formulæ.—From the above results, the following formulæ may be written, in which C = 0·01 per cent. of carbon, P = 0·01 per cent. of phosphorus, Mn = 0·01 per cent. of manganese, R = a variable to allow for heat-treatment, and the answer is the ultimate stress in lbs. per square inch. The coefficient of manganese in acid steel, called *x*, is the value given in Table VI., and applies only to contents above 0·4 per cent. The value of manganese in basic steel, called *y*, is the value given in Table VII., and applies to contents above 0·3 per cent.

TABLE VI.—MANGANESE.

Carbon.	Per cent. 0·42.	Per cent. 0·44.	Per cent. 0·46.	Per cent, 0·48.	Per cent. 0·50.	Per cent. 0·52.	Per cent. 0·54.	Per cent. 0·56.	Per cent. 0·58.	Per cent. 0·60.
	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.
0·10	160	320	480	640	800	960	1,120	1,280	1,440	1,600
0·15	240	480	720	960	1,200	1,440	1,680	1,920	2,160	2,400
0·20	320	640	960	1,280	1,600	1,920	2,240	2,560	2,880	3,200
0·25	400	800	1,200	1,600	2,000	2,400	2,800	3,200	3,600	4,000
0·30	480	960	1,440	1,920	2,400	2,880	3,360	3,840	4,320	4,800
0·35	560	1,120	1,680	2,240	2,800	3,360	3,920	4,480	5,040	5,600
0·40	640	1,280	1,920	2,560	3,200	3,840	4,480	5,120	5,760	6,400
0·45	720	1,440	2,160	2,880	3,600	4,320	5,040	5,760	6,480	7,200
0·50	800	1,600	2,400	3,200	4,000	4,800	5,600	6,400	7,200	8,000
0·55	880	1,760	2,640	3,520	4,400	5,280	6,160	7,040	7,920	8,800
0·60	960	1,920	2,880	3,840	4,800	5,760	6,720	7,680	8,640	9,600

TABLE VII.—MANGANESE.

Carbon.	Per cent. 0·35.	Per cent. 0·40.	Per cent. 0·45.	Per cent. 0·50.	Per cent. 0·55.	Per cent. 0·60.
Per cent.	Lbs. per sq. inch.	Lbs. per sq. inch.	Lbs. per sq. inch.	Lbs. per sq. inch.	Lbs. per sq. inch.	Lbs. per sq. inch.
0·05	550	1,100	1,650	2,200	2,750	3,300
0·10	650	1,300	1,950	2,600	3,250	3,900
0·15	750	1,500	2,250	3,000	3,750	4,500
0·20	850	1,700	2,550	3,400	4,250	5,100
0·25	950	1,900	2,850	3,800	4,750	5,700
0·30	1,050	2,100	3,150	4,200	5,250	6,300
0·35	1,150	2,300	3,450	4,600	5,750	6,900
0·40	1,250	2,500	3,750	5,000	6,250	7,500

Formula for acid steel, carbon by combustion:

$$40{,}000 + 1{,}000\,C + 1{,}000\,P + x\,Mn + R = \text{ultimate stress.}$$

Formula for acid steel, carbon by colour:

$$39{,}800 + 1{,}140\ C + 1{,}000\ P + x\,Mn + R = \text{ultimate stress.}$$

Formula for the basic steel, carbon by combustion:

$$41{,}500 + 770\ C + 1{,}000\ P + y\,Mn + R = \text{ultimate stress.}$$

Formula for basic steel, carbon by colour:

$$42{,}000 + 820\ C + 1{,}000\ P + y\,Mn + R = \text{ultimate stress.}$$

These formulæ are extremely useful in the management of rolling mills, etc., and may be used for quite a wide variety of steel sections.

CHAPTER VIII.

PHOSPHORUS.

THE condition in which phosphorus exists in iron and steel has been studied by Percy,[1] Schneider,[2] Cheever,[3] Juptner,[4] Stead,[5] and others. By far the most important of these investigations is that by Stead, which consists of a most careful chemical and metallographical determination of the various combinations that iron and phosphorus are capable of forming. Among the many important facts which he has clearly established are :

1st. That slowly-cooled iron is capable of holding in solid solution 1·7 per cent. of phosphorus, as phosphide, Fe_3P. Commercial wrought iron and steel containing low percentages of carbon contain the phosphorus in this condition.

2nd. The existence of the compound Fe_3P is placed beyond doubt. This compound and the above solid solution forms a eutectic mixture containing 10·2 per cent. of phosphorus.

3rd. Another chemical compound Fe_2P is formed, which gives rise to a second eutectic, with Fe_3P containing 15·58 per cent. of phosphorus.

The wonderful accuracy of Stead's work was confirmed by Saklatwalla[6] in his thermal investigation of the iron-phosphorus system, from which he constructed the constitution diagram (fig. 107). This diagram calls for no special comment, because its interpretation is self evident. It is, however, rather unfortunate that the details which have a direct bearing upon the question of steels are missing ; in other words, accurate determinations of the effect of phosphorus upon the Ar_3 and Ar_2 critical points are still needed.

As regards steels, the importance of Stead's work lies in the data he has published relating to the range of solid solutions containing less than 1·7 per cent. of phosphorus, and the effect upon these of increasing percentages of carbon.

Concerning the effect of phosphorus alone without the intervention of carbon, Stead says :—" In proportion as the phosphorus is increased from 0·0 to 1·7 per cent., specimens darken quicker when etched under the same conditions. The dimensions of the grains also become larger as the phosphorus is raised, and when about 1·0 per cent. is present cleavage faces more than an inch in diameter are frequently found in the fractured material.

---

[1] *Met. of Iron and Steel*, London, 1864, p. 64.

[2] *Oesterreichische Zeitschrift für Berg- und Huttenwesen*, 1886, p. 736 ; 1887, p. 362.

[3] *Trans. Amer. Inst. Mng. Engrs.*, vol. xv., p. 448 ; vol. xvi., p. 269.

[4] *Oesterreichische Zeitschrift für Berg- und Huttenwesen*, 1894, p. 208.

[5] *Journ. Iron and Steel Inst.*, 1900, No. 2, pp. 60-144.

[6] *Ibid.*, 1908, No 2, p. 92.

"The hardness of iron is steadily increased with each addition of phosphorus, until, when it is saturated and contains 1·7 per cent. of phosphorus, it takes a well-hardened drill to drill it properly. The saturated solution has a hardness of about 5·5 on Mohr's scale.

"Heat-tinting does not give gradation in colouring between the outside and centre of the grains, even when the phosphorus contained in them varies, but strong etching leaves the parts that were last to solidify relatively darker than the middle of the grains. Although the structure of pure iron and iron containing up to 1·7 per cent. of phosphorus shows a similar type of polygonal grains, there are certain differences in their etching properties. The polished surfaces of the phosphoretic metals, on being etched with exceedingly dilute nitric acid, were transiently prismatically coloured. The different grains

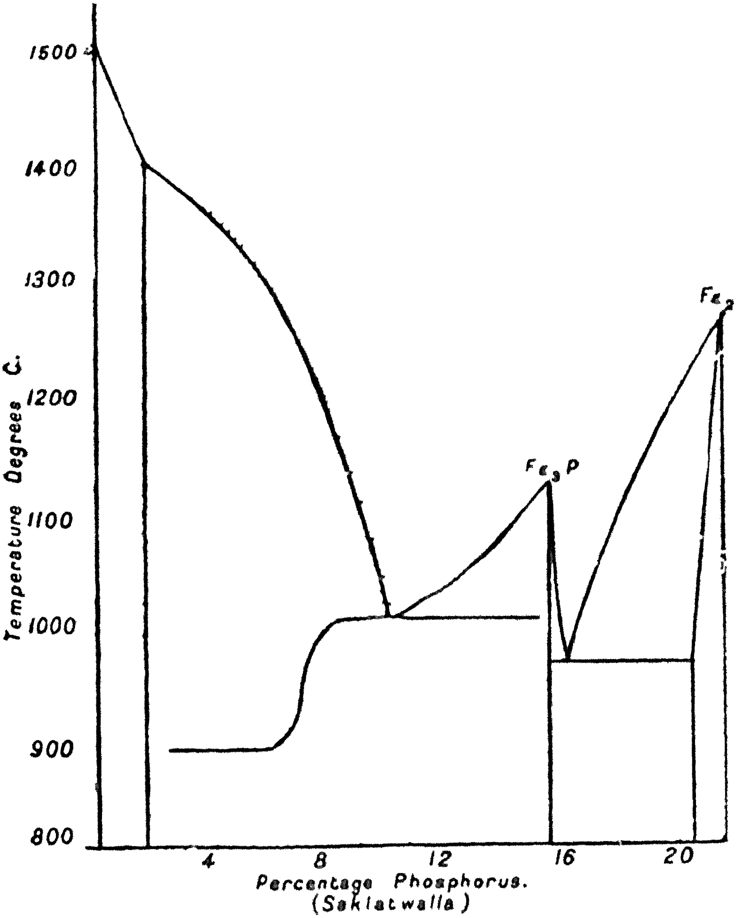


Fig. 107.

assumed different colours, and on a single specimen were to be seen grains coloured yellow, orange, red, purple, green, and blue. They changed rapidly from one colour to the others, and finally the colouring vanished with the continued action of the acid, and a brown stain or deposit was left on the surface, which eventually became black. This black matter could be removed from the surface by slight friction, and acid tincture of iodine partially destroyed it."

Stead also made a number of very instructive experiments, in order to determine the effect of carbon upon the affinity or solubility of phosphorus in the metallic solid solution. Some of the figures he obtained are given below (Tables VIII. and IX.) :—

TABLE VIII.

Nos.	Carbon.	Phosphorus.	Phosphorus as free Phosphide, Fe_3P.
	Per cent.	Per cent.	Per cent.
1	0·95	0·037	nil
2	0·96	0·099	0·002
3	0·95	0·122	0·035
4	0·96	0·347	0·065
5	1·02	0·548	0·163

TABLE IX.

Nos.	Carbon.	Phosphorus as free Fe_3P.	Phosphorus in Solution.	Total Phosphorus.
	Per cent.	Per cent.	Per cent.	
1	nil	nil	1·75	1·75
2	0·125	0·18	1·37	1·55
3	0·180	0·59	1·18	1·77
4	0·70	1·00	0·75	1·75
5	0·80	1·06	0·70	1·76
6	1·40	1·16	0·60	1·76
7	2·00	1·18	0·55	1·73
8	3·50	1·40	0·31	1·71

From these figures it is obvious that carbon has the effect of very materially decreasing the amount of phosphorus which can be held in solid solution by the iron, and causing it to separate as the phosphide of iron, Fe_3P. Further, it should be noted that the effect in this respect is even more marked than would be expected when the amount of free iron present is taken into account. If the free ferrite which exists in these mixtures were saturated with phosphorus, the alloy, No. 5, Table IX., after making allowance for the iron in combination as carbide, should contain 86·0 per cent. of ferrite (by weight), and, therefore, should be capable of holding 1·46 per cent. of phosphorus in solution. The actual amount found to be in solution was only 0·70 per cent. The difference is approximately the same proportion in the other samples, and is no doubt due to an imperfect state of equilibrium. Stead says :—"It is probable that if the mass in each case had been greater, and the cooling slower, the relative proportions of phosphorus thrown out of solution would have been different." Another disturbing factor is the difference in the solubility of the phosphorus when the steel is at temperatures just above and just below the Ar_1 or carbide change. Or, in other words, the solubility of phosphorus is no doubt different in the carbide solid solution or γ-iron than in α-iron.

No direct determinations have been made upon the amount of phosphorus which steel can dissolve when at temperatures just above the Ar_1 change, but useful deductions can be made from the data in Stead's paper. Thus, he concludes that a slowly-cooled pearlitic steel containing about 0·90 per cent. of carbon holds about 0·6 per cent. of phosphorus in solution. If, however, the ferrite contained in such a steel were saturated with phosphorus it should be capable of holding about 1·4 per cent. by weight. The actual figure, 0·6 per cent., therefore, seems to be governed by the condition—that is, the amount of phosphorus which existed in solution just before the carbide change. When more phosphorus is present the excess separates in the form of Fe_3P as the cooling proceeds to the Ar_1 point, and, after that change has occurred, the excess of phosphide is only taken in solution by the ferrite by keeping the mass at a temperature just below the Ar_1 for a prolonged time.

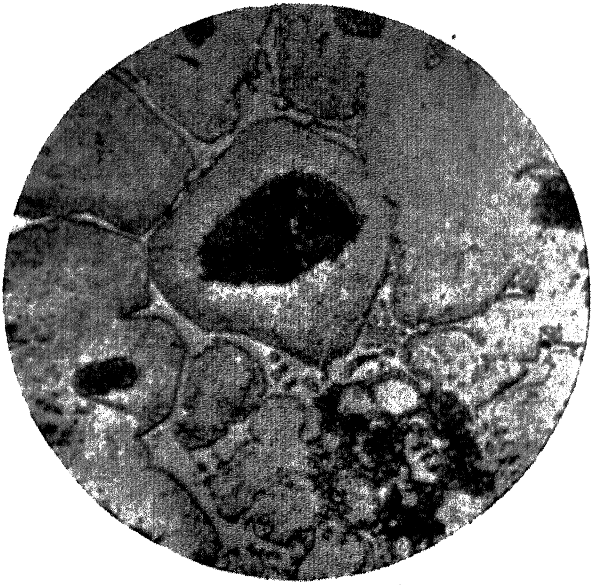


Fig. 108.—White Matrix = Phosphide of Iron, Fe_3P. × 150.

It is known that phosphorus raises the temperature of the carbide change, a fact which indicates that this element is less soluble in the solid solution than in the products of its decomposition.

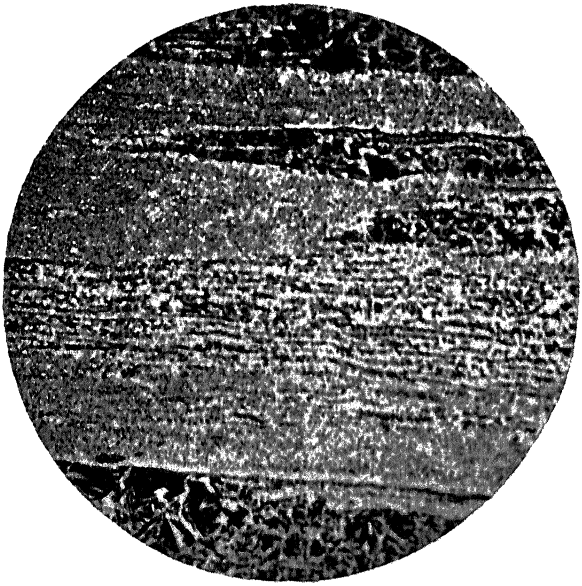


Fig. 109. Phosphorus Segregation. × 150.

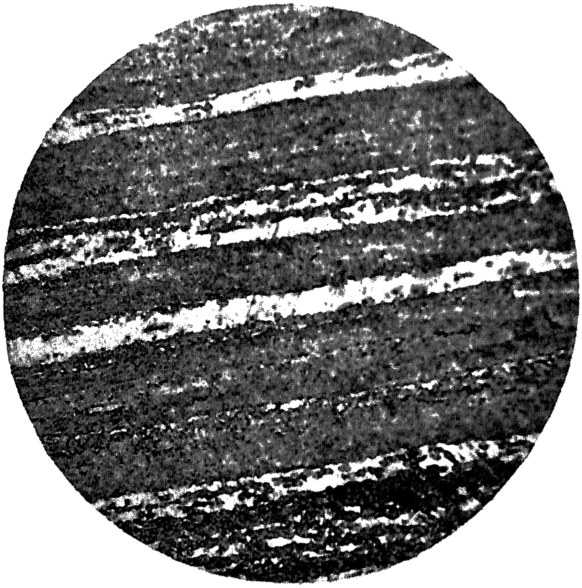


Fig. 110.—Phosphorus Segregation in Steel Bar. White Bars = Areas rich in Phosphorus, from which the Carbon has been almost completely expelled. × 150.

Fig. 109 very clearly illustrates the fact that the critical points of steel are raised by the addition of phosphorus. It was taken from a segregated portion of steel bar, and was cut at right angles to the direction of rolling. The segregate in this instance was originally located between groups of crystals, and in consequence the phosphorus rich areas are irregularly distributed throughout the mass. The bar had been somewhat overheated, and showed a coarsely crystalline, or what is sometimes called a granular fracture. After heating a piece of the steel for two hours at 800° C., the structure of the parts containing low phosphorus became refined—*i.e.*, the crystals became much smaller, indicating that they had passed through the critical points, whilst those high in phosphorus remained unchanged (see the darker areas with relatively large masses of pearlite). The effect of phosphorus in expelling the carbon from areas high in phosphorus is shown in fig. 110. In this case the steel was heated to 900° C. for two hours, and then slowly cooled. The photograph was taken from a longitudinal section, and the white bands indicate the direction of rolling. These white bands contain very little carbon, it having been removed or expelled by the relatively high percentage of phosphorus they contain.

When segregation is taking place during the solidification of a steel ingot, the liquid which is last to solidify—that is, the segregate—always contains more carbon as well as phosphorus than the part which solidified at an earlier stage. Stead has, however, shown that once the mass is perfectly solid but still at temperatures about its highest recalescence point, the carbon begins to diffuse from the areas rich in phosphorus to those containing less of that element. When this diffusion is complete the phosphoretic parts are practically free from carbon.

Phosphorus seems to accelerate the rate at which the crystals of steel grow when at temperatures above the critical points, and it is no doubt owing to this action that this element renders steel much more sensitive to overheating.

Even if it were not generally recognised, it would be obvious from Stead's work that the deleterious effect of phosphorus in producing cold shortness and brittleness becomes greater as the percentage of carbon contained in a steel is raised. This is due to the fact that, as the carbon contained in steel is raised, the amount of free ferrite present diminishes, and since the phosphorus is only dissolved in ferrite, it becomes concentrated in that constituent as the carbon content is raised. Thus, the effect upon the ferrite of 0·04 per cent. of phosphorus in a steel with 0·90 per cent. of carbon is equivalent to that of 0·046 per cent. in a steel with only 0·20 per cent. of carbon. Judging from Dr. Stead's figures, the practical effect in this connection must be even more serious than would be theoretically expected, because the amount of free phosphide of iron very rapidly increases as the carbon content is raised.

CHAPTER IX.

SULPHUR.

Sulphur is one of the unavoidable impurities which is present in all commercial steels. Its effect upon the properties of the metal is, broadly speaking, considered to be injurious, but in very many instances it is not so. The percentage of sulphur is, however, generally kept as low as is practicable, but the permissible quantity largely depends upon the purpose for which the material is required, and also upon the kind and degree of mechanical treatment it is subjected to in the rolling and hammering operations. For some special engineering purposes the sulphur must be below 0·04 per cent., but for ordinary constructional steel 0·06 per cent. is generally allowed, and as much as 0·08 per cent. or more is known to have no serious effect if sufficient manganese is present.

Probably the most objectionable feature of abnormal quantities of sulphur is the tendency to render the mass "red short" or brittle whilst it is hot. This property is, however, one which almost invariably gives the manufacturer much more trouble in the rolling mill than it is likely to give the user, and consequently makes him anxious to keep the percentage within reasonable limits. The actual amount of sulphur contained in steel is not the only factor which governs its influence, the condition in which it exists therein is of even greater importance.

Sulphur may be present in steel in two distinct chemical forms. Professor Arnold[1] first demonstrated that in steel containing no manganese the sulphur exists as ferrous sulphide, FeS, and later he showed that in the presence of an excess of manganese the whole of the sulphur is present as sulphide of manganese, MnS. These two chemical compounds possess totally different mechanical characteristics, and, therefore, impart different properties when present in steel. Manganese sulphide is, for instance, plastic at forging temperatures, and can be readily elongated without being fractured when the metal is being rolled. On the other hand, the presence of iron sulphide is absolutely fatal to the forging properties of steel. This remarkable influence of manganese in neutralising the evil effects of sulphur was very clearly brought to light in the experiments made by Brinell in 1897.[2] He found that steel containing as much as 0·56 per cent. of suphur along with 1·06 per cent. of manganese could be easily rolled, and further, that the mechanical properties of the metal when tested in the direction of rolling were at least equal to those of a steel with about the same carbon content, but containing exceedingly low percentages of sulphur. From results he obtained with a steel containing—

---

[1] *Journ. Iron and Steel Inst.*, No. 1, p. 129.

[2] *Journ. Iron and Steel Inst.*, 1901, No. 2, p. 234.

Carbon,	0·31 per cent.
Silicon,	0·126 ,,
Manganese.	0·94 ,,
Sulphur,	0·150 ,,
Phosphorus.	0·033 ,,

He concludes :—" Although here, too, the percentage of sulphur far exceeds the ordinary limit, the adoption of this description of steel for practical purposes is by no means precluded on this account. . . . The tensile properties of this metal proved to be quite satisfactory in the direction of rolling, and the hardening properties were found to be unexceptional. The material was superior with regard to resistance to impact to any of the low sulphur steels. This was the case in every kind of test, whether in the hardened or unhardened state, at a low or a high temperature, or whether the specimens were notched or normal."

From the foregoing remarks it is almost unnecessary to emphasise the importance of having sufficient manganese in steel to ensure that all the sulphur exists as manganese sulphide, or that none should be present as sulphide of iron. Owing to segregation, etc., this state of affairs cannot safely be attained by merely arranging that the ratio of manganese and sulphur in the steel conforms to that of the formula MnS. In other words, even if there is enough manganese present to combine with the whole of the sulphur, its unequal distribution may leave some sulphur free to form iron sulphide.

Sulphide enclosures and segregation can be detected without the aid of the microscope. The method which was first described by Heyn and Bauer[1] is as follows :—The specimen is first roughly polished, and a piece of silk, which has previously been dipped in a solution of hydrochloric acid and mercuric chloride, is carefully spread over the surface, and allowed to remain in contact for about five minutes. The solution should contain about 10 grammes of mercuric chloride, 20 c.c. of hydrochloric acid (1·124), and 100 c.c. of water. The acid attacks the sulphide areas, with the formation of H_2S, and this precipitates black mercuric sulphide from the mercuric chloride solution with which the silk is impregnated. The sulphur prints thus obtained are coloured to a varying degree, according to the distribution of sulphur. They are very useful in determining what section of the specimen should be reserved for more detailed examination under the microscope. A similar method is to use silver bromide photographic paper which is first wetted with dilute sulphuric acid and then placed on the polished surface of the steel. In this case also the sulphuretted hydrogen which is liberated from the sulphides blackens those parts of the bromide paper with which they are in contact.

Manganese sulphide can be readily detected under the microscope as a dull grey or dove-coloured constituent in the form of globular or irregular-shaped areas. In sections that have been polished at right angles to the direction of rolling, this constituent appears as small specks, which are often

---

[1] *Bericht des Materialprüfungsamtes*, 1906, vol. xxiv.

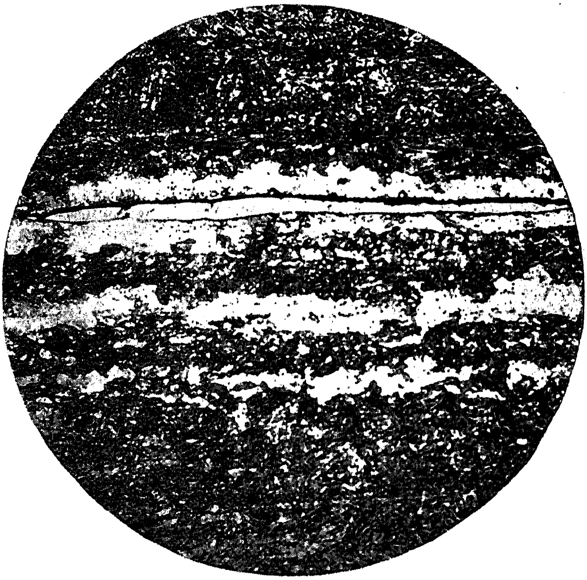


Fig. 111.

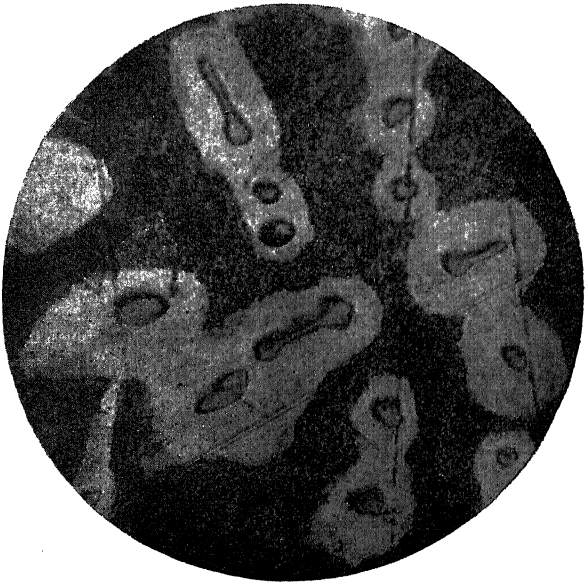


Fig. 112.

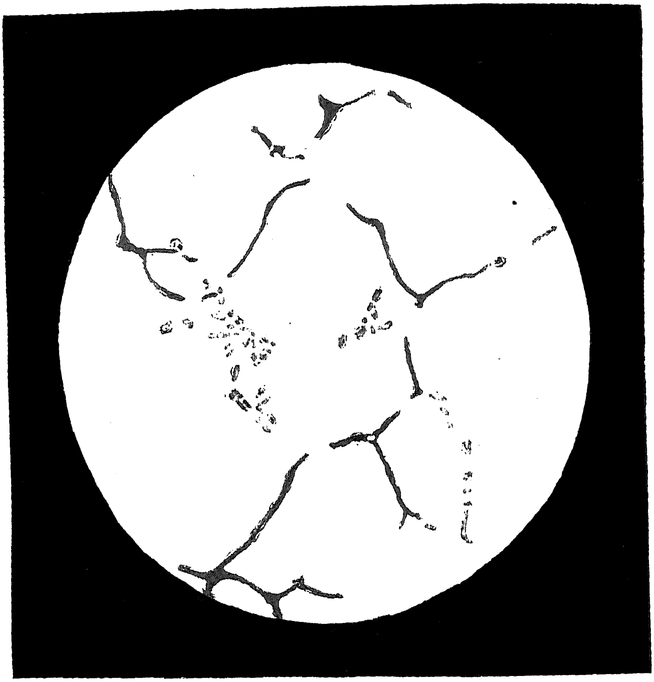


Fig. 113.—Aluminium Ingot No. 1408. Manganese, 0·41 per cent.; Sulphu 0·53 per cent. Magnified 490 diameters and reduced by one-half. (*Arnol* and *Bolsover.*)

difficult to see, but, on account of the elongation during rolling, they appear as long bars when the polished surface has been cut parallel to the direction of rolling. Fig. 111 shows an elongated patch of manganese sulphide. The same constituent is also shown in fig. 112, which represents a locally segregated area in a slowly-cooled steel casting.

Sulphide of iron, when viewed under the microscope, is pale yellow or yellowish-brown, which may be embedded along with or juxtaposed to sulphide of manganese. Unless great care is taken in the examination of microsections containing these two sulphides, it is a very difficult matter to distinguish them, especially when only small quantities are present. Both are shown in fig. 113 (frontispiece), which has been reproduced from a paper by Professor Arnold and Mr. G. R. Bolsover.[1]

In an excellent paper dealing with this subject, Mr. G. Röhl[2] says:— "It is very often difficult (if not quite impossible in the case of small enclosures), especially in the case of manganese sulphide, to correctly recognise the tint." Mr. E. F. Law[3] also says that "the sulphide occurring in steel varies very much in colour and composition. In some steels it is so pale in colour that it is difficult to photograph, whereas in others it is so dark that it may easily be mistaken for manganese silicate."

According to Matweieff,[4] the two sulphides can be distinguished by etching with tartaric acid when the ferrous sulphide becomes darkened while the manganese sulphide remains unchanged. By using a 1 per cent. solution of picric acid in alcohol Röhl obtained a similar darkening of the iron sulphide, the time of etching being about three minutes. Le Chatelier[5] observed that by using a 5 per cent. solution of picric acid in alcohol veins are developed in the ferrite which connect up the various ferrous sulphide areas; these lines are no doubt due to traces of sulphide existing in the ferrite grains.

Ferrous sulphide solidifies at 1,188° C., and this temperature being considerably below that at which the mass, even in the case of high carbon steels, becomes completely solid, the sulphide is squeezed to and solidifies at the boundaries of the crystals. These sulphide boundaries or patches then form bases upon which the ferrite that subsequently separates from solid solution tend to grow. This has been drawn attention to by Dr. Rosenhain,[6] and is very noticeable in slowly cooled steel castings (see fig. 112). The presence of sulphides in the form of a more or less continuous network, and surrounded or supported by almost pure ferrite, is most undesirable in steel castings which may be subjected to sudden stresses. The object of annealing or refining is to bring about a recrystallisation of the mass and regular distribution of the carbon (see figs. 123 and 124, Chap. X). By heating just above the temperature at which the whole of the carbon and iron form a homogeneous solid solution, followed by slow cooling, the network of ferrite and sulphide get completely broken up, and the ductility of the metal is very much improved. Röhl has found that the freezing

---

[1] *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 396.

[2] *Journ. Iron and Steel Inst.*, 1912, Carnegie memoir, p. 28.

[3] *Ibid.*, 1907, No. 2, p. 94.

[4] *Revue de Metallurgie*, 1910, p. 447.

[5] *Bulletin de la Société d'Encouragement*, Sept. 1902.

[6] *International Association for Testing Materials*, 1909, No. 5

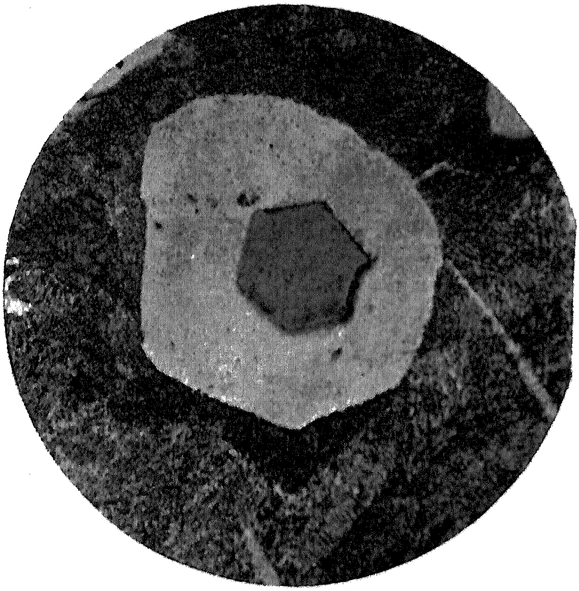


Fig. 114.

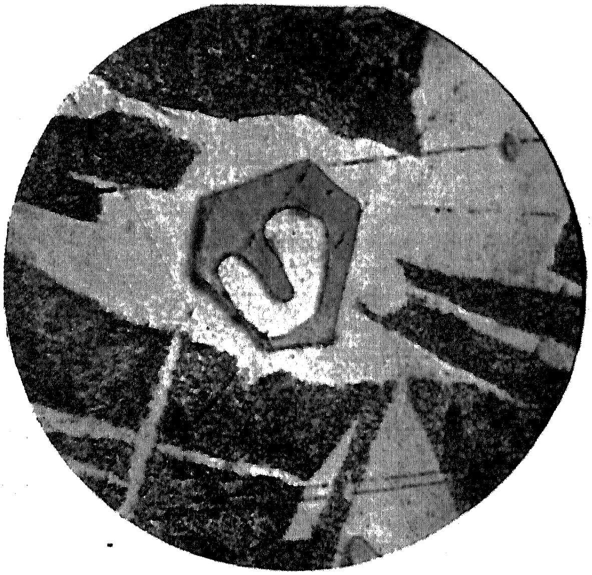
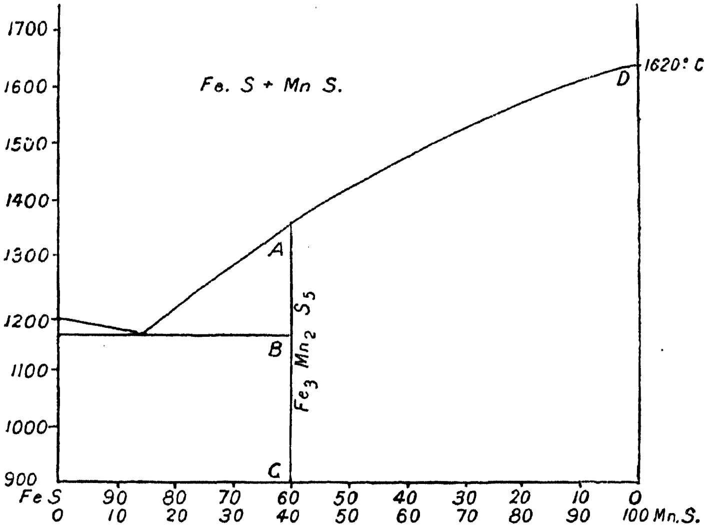


Fig. 115.

temperature of pure manganese sulphide is 1,620° C., which is considerably higher than that of pure iron (1,505° C.). The melting point diagram and constitution of the iron-manganese sulphide system has not been determined, and it is, therefore, impossible to decide whether there is a eutectic or not, or even at what temperature solidification of the manganese sulphide, contained in steels, takes place. Indeed, Röhl's investigations seem to indicate, as Dr. Stead suggests,[1] that manganese sulphide does not solidify in the pure condition from liquid steel, but in the form of a solid solution of $Mn_3Fe_2S_5$ along with MnS, and that as the mass slowly cools the double compound becomes unstable, and the manganese in the surrounding steel replaces the iron in combination with the sulphur. From the available evidence, it is uncertain whether this view is correct. This would mean that at very high temperatures the affinity of the iron when in large quantities is sufficient to partly overcome that of manganese for sulphur, and that at lower temperatures or at a certain definite critical point the influence of the manganese predominates.



(Röhls' diagram)

Fig. 116.

If this is really what occurs it would account for the fact that what is generally regarded as manganese sulphide frequently possesses different tints when viewed under the microscope, or these variations may be due to differences in the composition of the solid solution between $Mn_3Fe_2S_5$ and MnS. Further, it may be the cause of the dove-grey sulphides solidifying in a variety of forms in cast steels containing different proportions of manganese and sulphur. As previously indicated, these enclosures often take the form of a more or less complete meshwork, when they must clearly have solidified at a later period than the other portions of the steel. In other cases, however, they take a well-defined crystalline form (see figs. 114 and 115), when they must have solidified at a much earlier period, and probably before the steel as a whole had commenced to solidify, or at least whilst it was still pasty.

---

[1] Discussion on Arnold and Bolsover's paper.

Röhl's diagram for the sulphide system, FeS + MnS, is shown in fig. 116. It is important to note that Röhl gives no definite evidence for supposing that the line A B C (fig. 116) corresponds to a definite double compound of the two sulphides. In fact, all the experimental observations would be satisfied if the line A B C were eliminated from the diagram and a sloping line drawn from the point B to meet the point D. B would then indicate the saturation point of FeS in solid MnS.

CHAPTER X.

BURNING AND OVERHEATING STEELS.

THE terms "burnt" and "overheated," which are frequently used in the steel trade, are often employed in such a general sense that it is difficult to attach any real significance to their application. It may, however, be taken for granted that when a steel is said to be burnt its properties do not come up to expectations. Even in the most carefully managed works, steel may occasionally get overheated or burnt, and if it gets into a user's hands it may give rise to considerable trouble. It should be remembered, however, that manufacturers are not always the culprits in this connection, and it frequently happens that a steel of excellent quality is ruined by careless heating at the hands of the consumer.

The exact nature of the changes which take place, and even the precise meaning of the terms "burnt" and "overheated" were for a considerable time very imperfectly understood.

A committee of the Iron and Steel Institute[1] on the nomenclature of metallography defines "overheated" as "applied to steel that has been heated to excess and not quite burnt."

The term "burnt" is defined as follows: "Applied to metal which is brittle in consequence of an alteration of its mass caused by excessive heating. Recent study has shown that a so-called burnt steel is not necessarily oxidised in its mass. Near to the external surface, if carbon is low or absent, intergranular layers of oxide of iron may sometimes be detected. The chemical composition is not necessarily altered by the so-called burning. Steel may, on heating to a very high temperature in an inert atmosphere, develop, after cooling, many of the properties of burnt steel. Burnt steel is generally coarsely granular, and is easily fractured."

Professor Howe[2] states: "Steel which has been exposed to a very high temperature is known as 'burnt.' It is cold-short and brittle, can be forged and welded only with care, and has a low tensile strength. Its fracture is coarse and even flaky, crystalline, with brilliant facets. Steel known as 'overheated' has a coarse structure, which may be removed more or less completely by reheating or careful forging. Excessively long or strong overheating produces the structure known as 'burnt,' and the coarseness and brittleness due to burning are removed with greater difficulty, and much less completely than those due to overheating, yet in the same manner and by the same expedients."

Professor Stansfield[3] says:—"The term burning as applied to steel arises, no doubt, from the appearance of scintillating sparks which often accompany serious overheating of steel." He defines overheating as "reheating to below the point of incipient fusion," and says that "steels that have been merely overheated can be completely restored by heating just above their highest recalescence point and allowing to cool."

---

[1] *Journ. of Iron and Steel Inst.*, 1902, No. 1.

[2] *Metallurgy of Steel.*

[3] *Journ. of Iron and Steel Inst.*, vol. xi., 1903.

Dr. Stead[3] says :—"Confusion appears to have arisen by confounding 'burnt' with 'overheated' steels." He gives a concise definition of each term. "Overheating is heating at any point below that which produces incipient disintegration, and results in the formation of large crystals." "Burning is heating at or above the point at which such disintegration occurs; burnt steel is nearly always coarsely crystalline."

Early in his researches Stansfield was led to connect the phenomena of burning with the actual fusion of part of the steel, and the data he obtained, and also that published by Stead, amply confirm that view. Therefore, knowing that the temperatures at which steels begin to melt are lower the greater the carbon content, it follows that the burning temperatures are lowered in the same way.

In the operation of heating the physical changes that occur in steel are exactly the reverse of those that take place on cooling. When heated to a temperature just above the Ac_1, Ac_2, and Ac_3 points the whole of the carbon and iron exist as a homogeneous solid solution of carbide of iron in γ-iron. At first these crystals of solid solution are exceedingly small, but as the temperature is further raised or the time is prolonged some of them grow at the expense of those surrounding them. There is no doubt that crystal growth begins immediately the temperature is raised above the highest critical point of any particular steel, but from a practical point of view the rate of this growth is more directly influenced by raising the temperature still higher. It is impossible at present to lay down any definite rule indicating the precise temperature at which the crystals begin to grow at what may be regarded as a dangerous rate, because this is also affected by the carbon content of the steel. Further, in addition to the time factor, the mass has also to be taken into consideration on account of its influence upon the subsequent rate of cooling. Still another consideration of considerable importance is the amount of deformation or work, if any, that is put upon the steel after the heating.

Crystal growth continues as steel is heated up to the temperature at which it begins to melt, when the liquid which is then formed contains much more carbon than the average of the steel. The phosphorus and sulphur also become concentrated in the molten portion. At first the liquid exists in the form of infinitely small globules throughout the crystals, very much in the same manner as the initial separation of water from an atmosphere which is super-saturated with aqueous vapour. These minute globules coalesce, forming relatively large drops, which, owing to the attractive forces between the solid units of the crystals, are squeezed to the boundaries, and form a complete liquid envelope around the crystals. This is illustrated in fig. 117, where the white areas represent the parts of the specimen that were liquid at the temperature from which it was quenched. When this stage is reached the conditions are most favourable for the liberation of any dis-

---

Journ. of Iron and Steel Inst., 1905, No. 2.

solved gas which the steel may contain, and it is the sudden evolution of gas under these conditions which causes the characteristic scintillation of burning steel. The blisters which are formed in many burnt specimens of steel are also caused by the gas bubbling through the liquid surrounding the crystals.

It has been demonstrated by Stead that the embrittling of steel after burning is not caused by the relatively high carbon content of the liquid which is formed at the burning temperature, because on again cooling this carbon quickly diffuses back into the crystals. Indeed, when the steel is cooled through the Ar_3, Ar_2 critical points a large proportion of the ferrite which is then deposited from the solid solution finds its way to the crystal boundaries, or in much the same position that the original high carbon liquid occupied. Stead considers that the brittleness is due to the phosphorus

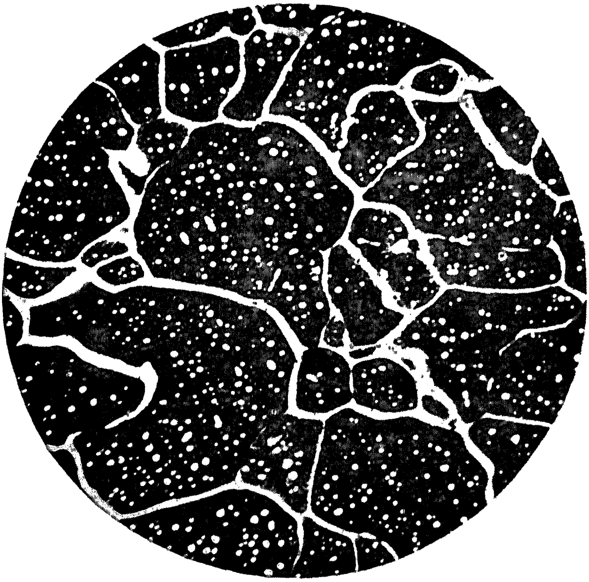


Fig. 117.—Quenched from Burning Temperature. White Areas correspond to Parts that were Liquid. × 150.

which becomes concentrated in the liquid envelope not diffusing back into the solid as the steel is cooled from the burning temperature. He says :—"If the burning has been very severe, the white carbon free envelopes are sometimes very rich in phosphorus, and on etching with picric acid in water they rapidly become darkened—a proof of the presence of the phosphorus. It is well known that on removing the oxide of iron scale, which forms on steel which has been correctly heated, the surface of the metal is perfectly smooth and clean, presenting no indication of cracks. If the steel be, however, heated to the burning temperature—*i.e.*, to the temperature at which it begins to melt, when it becomes brittle—after removing the scale the surface of the metal is seen to be covered with little blisters. If the steel when in this condition be rolled, hammered or strained in any way, cracks

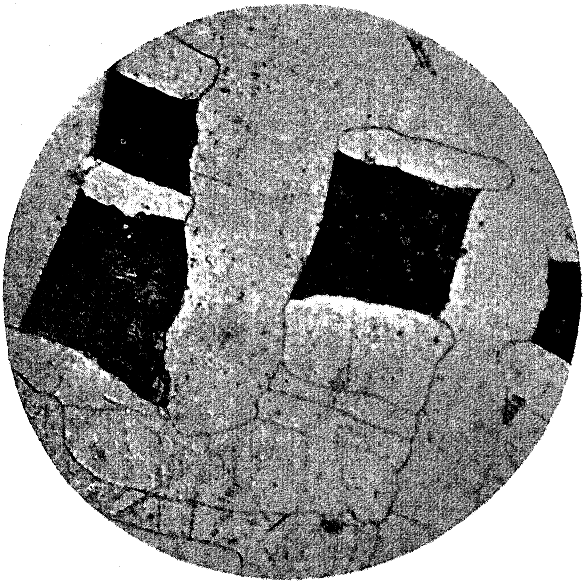


Fig. 118.—Overheated Mild Steel. × 150.

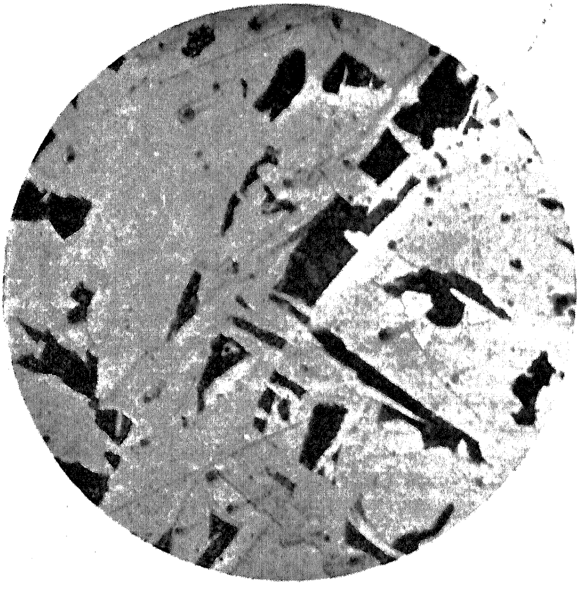


Fig. 119.—Overheated Steel. × 150.

are immediately formed at the crystal junctions of the metal, and the freshly exposed surfaces become coated with a film of oxide of iron. It is these deposits, so common in slightly worked burnt steel, that has led to the erroneous conclusion that oxygen finds its way between the crystal joints of the solid metal. Much careful research during the last ten years has led me to conclude that during the heating in the furnace, unless the material is distributed or shaken, there can be no internal oxidation of the iron and no inter-crystalline formation of iron oxide, that oxide of iron is only formed in the envelope, and it is only after the formation of fissures or incipient separation of the crystals by strain that oxygen can enter below the skin."

The brittleness which is caused by overheating is revealed in test specimens by a diminution in the ductility as shown by a decreased elongation, contraction of area at the fracture, resistance to shock and fatigue, and a coarsely crystalline or what is often termed a granular fracture. From what has been said above, it is obvious that this is not due to any change of chemical constitution, but to the fact that there has been an alteration in the internal arrangement of the constituents, ferrite and pearlite. After overheating these constituents exist in the metal in much larger patches. This coarsely crystalline structure can be removed and the normal properties of the steel restored simply by reheating the mass to slightly above the temperature of its highest recalescence point, followed by slow cooling. The structures of three different overheated steels are shown in figs. 118, 119, and 120, and the structures seen in figs. 121 and 122 were taken from the same specimens as figs. 119 and 120 after refining or heating to 900° C., and then slowly cooled.

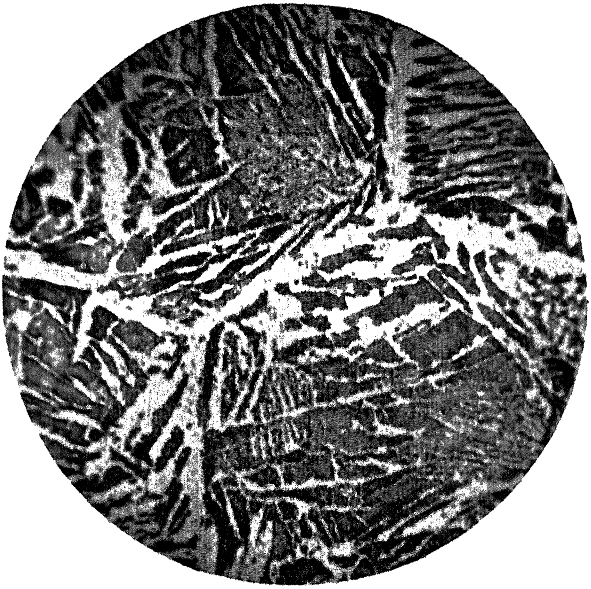


Fig. 120.—Overheated Steel. × 150.

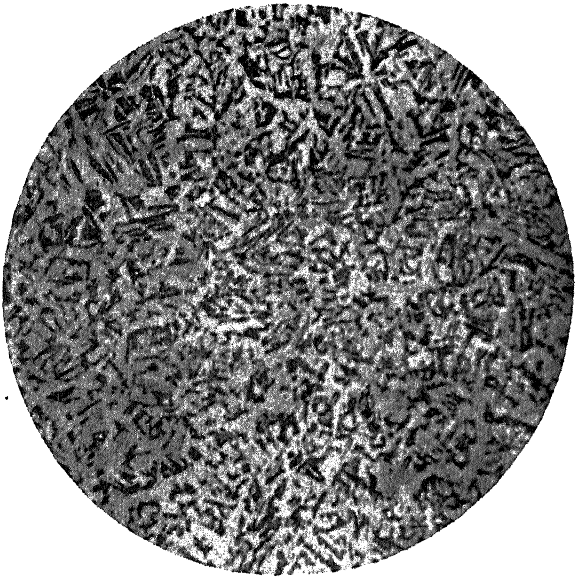


Fig. 121.—Same Specimen as Fig. 119 after Refining. × 150.

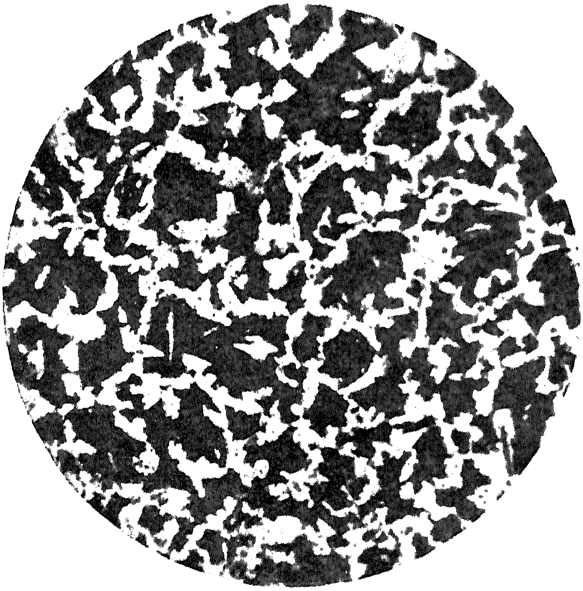


Fig. 122.—Same Specimen as Fig. 120 after Refining. × 150.

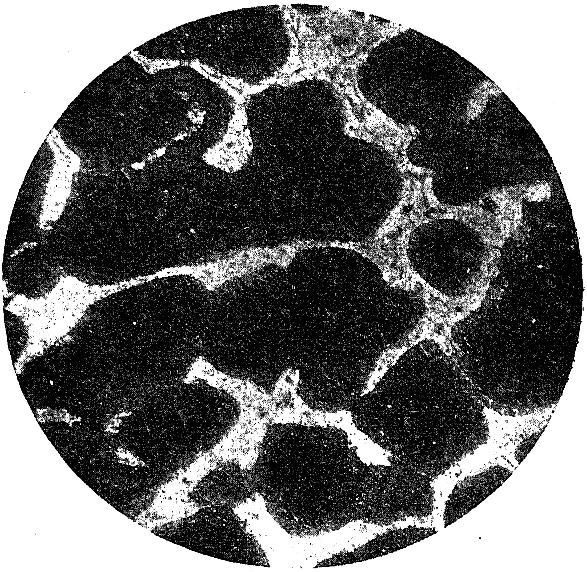


Fig. 123.—Structure of Cast Steel. × 150.

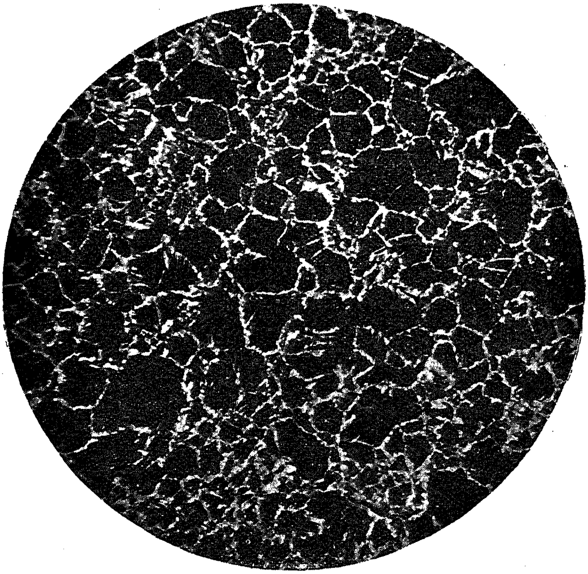


Fig. 124.—Same Specimen as Fig. 123 after Annealing. × 150.

This refining of the structure is caused by the recrystallisation, which occurs as the metal passes through the critical ranges of temperature. The most probable explanation of this operation is as follows:—Starting with an overheated steel possessing a structure as shown in fig. 118, on heating to just above the Ac_1 point, the dark pearlitic areas become transformed into the γ-iron solid solution. Each of those areas do not, however, possess a uniform orientation—*i.e.*, consist of one crystal—but of a very large number of minute crystals of differing orientation. This recrystallisation on heating is in many ways similar to the formation of small crystals from a liquid as it passes through its freezing temperature. When the steel is further heated the initial crystals of the solid solution which contain 0·9 per cent. of carbon become capable of holding more iron in solution. Hence the ferrite surrounding these crystals is progressively taken into solution as the temperature is raised. Redistribution of the ferrite and carbon proceeds in this way, by diffusion, until the temperature of the highest recalescence point is reached, when the carbon is uniformly distributed through the mass. Whilst the steel is then of the same constitution as it was during the time of overheating, owing to the recrystallisation which occurred on heating through the Ac_1 point and upwards, it possesses an infinitely finer crystalline structure. Hence, when the metal is again cooled these small crystals behave quite independently by depositing the ferrite they contain in relatively small masses, and finally leaving only small areas of pearlite.

It has been shown by Stead that the properties of rather low carbon steels which have been burnt can be restored by the same heat-treatment as that for overheated steels.

It should be noted at this stage that there is a decided feeling amongst metallurgists who have to deal with carbon tool steel containing 0·9 per cent. of carbon or more, that when such steel is overheated it gives what is known as a "dry fracture," which cannot be removed by heat-treatment or mechanical work.

The brittleness of overheated steel is largely, if not entirely, due to the lack of grip or intercrystalline penetration of the metal.

The operation of refining overheated steel is fundamentally the same as that of annealing steel castings.

The microstructure of a steel casting is shown in fig. 123, where the brittle sulphide of manganese can be seen running through the white ferrite areas. The structure of the same steel, after heating to 900° C. followed by slow cooling, is shown in fig. 124. This treatment has refined the structure of the metal, and whilst the sulphide of manganese is still present, it can scarcely be detected at a magnification of 150 diameters, and its embrittling effect is reduced to a minimum.

CHAPTER XI.

THE DEFORMATION AND STRAIN HARDENING OF METALS.

One of the most useful properties possessed by metals is the facility with which they undergo plastic deformation when pressed, hammered, or rolled. Until a comparatively short time ago it was generally supposed that this change of shape was brought about very much in the same manner as the deformation of such pasty substances as putty and soft pitch when subjected to unequal pressures. But, as a result of the many investigations made by Professor Ewing and Dr. Rosenhain,[1] it has been conclusively demonstrated that the deformation of metals under strain is accompanied by a process of direct slipping along the gliding planes or surfaces of the numerous crystals contained in the metallic mass. It has been shown by the above-

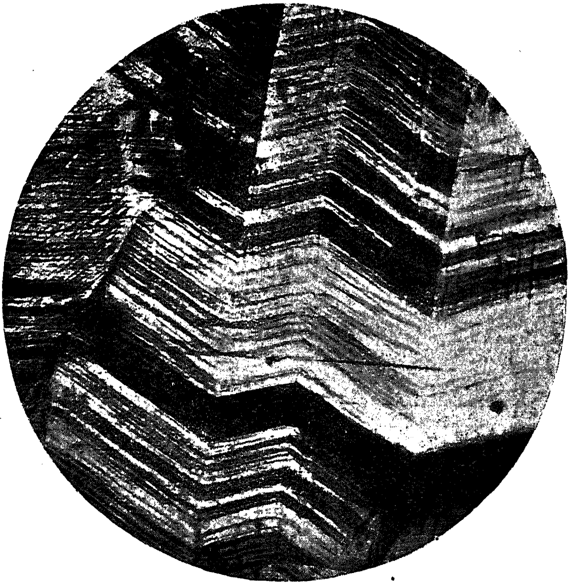


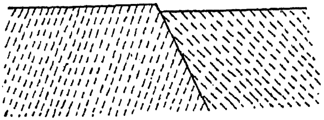
Fig 125.—Showing Slip Bands passing through Twin Crystals. × 150.

---

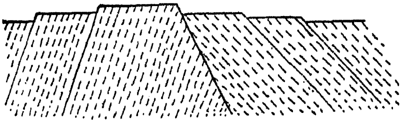
[1] "The Crystalline Structure of Metals," *Phil. Trans.*, 1900, p. 353; 1901, p. 279. "Experiments on Micro-Metallurgy—Effects of Strain," *Proc. Roy. Soc.*, 1899, vol. lxv., p. 85.

mentioned observers that evidence of this slipping can be readily seen by first carefully polishing the surface of a metal and then straining it sufficiently to produce permanent deformation. An examination under the microscope will then reveal a number of lines running in different directions on the various crystals (see fig. 125). The lines have been described by Ewing and Rosenhain as "slip bands." The nature of this slipping will no doubt be more readily understood from the diagrammatic illustration given in fig. 126. When metals are deformed in the cold state, they become much harder.

This hardening is generally referred to as strain hardening. Various theories have, from time to time, been advanced to explain this particular kind of hardening. At first sight it would appear that this is merely due to the mass becoming more compact, and consequently less easy to penetrate or pull apart. Simple as this explanation is, modern research has conclusively proved that it is quite inadequate, though it certainly contains some truth. Another explanation is that the mechanical deformation produces smaller crystal grains, and the increased hardness is due to the crystalline fineness of structure.



Before Straining.



After Straining.

Fig. 126.—Diagram illustrating the Effect of Strain upon Metals (*Ewing* and *Rosenhain*).

The theory which now seems to be most generally accepted is that advanced by Dr. Beilby. There is, however, another, due largely to Professor Tammann, which cannot be entirely overlooked. Most of Dr. Beilby's work[1] has been summarised in a lecture which he gave before the Institute of Metals, May 12th, 1912. In that lecture he said:—"In the operation of polishing a true skin is formed over the polished surface. This skin gives unmistakable signs that it has passed through a state in which it must have possessed the perfect mobility of a liquid. In its final state it possesses distinctive qualities, which differentiate its substance very clearly from that of the unaltered substance beneath it. It is, for instance, much harder, and, even when formed on the surface of a crystal on which the hardness varies in different directions, its hardness is the same in all directions. The discovery that layers of a solid, many hundreds of molecules in thickness, can have the mobility of the liquid state conferred upon them by purely mechanical movement, opened up a new field of inquiry into the internal structure of metals which have been hardened by cold working. As a result of this inquiry a theory of the hard and soft states was suggested. According to this theory, hardening results from the formation at all the surfaces of slip or shear of mobile layers similar to those produced on the outer surface by polishing. These layers only retain their mobility for a very brief period and then solidify in a vitreous amorphous state, thus forming a cementing material at all surfaces of slip or shear through the mass. In the use now made of the term amorphous, it means non-crystalline in the most intimate sense of the word; in this state molecules are not marshalled in crystalline order and orientation. The addition of the qualifying term "vitreous" narrows the field to substances which in some degree resemble the glass-like form assumed by the silicates when they are solidified from the molten state."

---

[1] "Surface Flow in Crystalline Solids under Mechanical Disturbance," *Proc. Roy. Soc.*, 1903, vol. lxxii., p. 218. "The Hard and Soft States in Metals," *Philosophical Magazine*, 1904, p. 258. "Surface Structure of Solids," *Soc. Chem. Ind.*, Liverpool, 1903. "The Hard and Soft States in Metals," *Faraday Society*, June 9, 1904. "The Hard and Soft States in Ductile Metals," *Proc. Roy. Soc.*, 1907, A, vol. lxxix., p. 463. "Influence of Phase Changes on the Tenacity of Ductile Metals at the Ordinary Temperature and at the Boiling Point of Liquid Air," *Proc. Roy. Soc.*, 1905, A, vol. lxxvi., p. 462.

This theory has been opposed chiefly by Professor Tammann[1] on the ground that it involves a violation of the phase rule, and also because it does not account for the difference between the action of uniform (hydrostatic) pressures, and of pressures causing flow.

The answers to these objections have been extensively dealt with by Dr. Rosenhain.[2] According to the phase rule, the liquid of a pure metal can exist in contact and in equilibrium with its own solid only at one particular temperature—viz., the freezing temperature, when the pressure is constant. The rule makes no stipulation as to the time it is necessary to allow for any unstable phase to be converted into its stable variety. Therefore, if it can be demonstrated that an unstable phase or constituent does in the slightest degree, and at any temperature within its unstable range, tend to be converted into the stable condition, the requirements of the phase rule are amply satisfied. In actual practice it may, and indeed under certain conditions it does, take an almost indefinite number of years for the whole of a transformation to be completed. In most cases the velocity of this kind of change is at a maximum, when the mass is at a temperature not very much below that of the normal inversion temperature, but in some the tendency for an unstable phase to take up its more permanent form increases as the temperature is raised to just below the critical change point. Dr Beilby's theory is, therefore, in no way opposed to the phase rule. The well-known amorphous substance glass, as it is commonly used, is in an unstable state, from the point of view of the phase rule, because at the ordinary temperature it should be in the crystalline form to be in a perfectly stable condition. In the discussion on a paper by Professor Carpenter and the author,[3] Dr. Beilby has placed on record certain theoretical reasons for considering that the amorphous condition, though it occupies a larger volume—that is to say, it is less dense than the crystalline state—should, nevertheless, possess a greater degree of hardness. It is rather significant to note that the high pressure jets of water that are used in hydraulic mining operations are so hard that it is impossible to cut through them with a two-handed steel saw. This kinetic hardness is caused by the increased number of molecules that are passing through a given space per unit of time. The increased hardness of the amorphous material which is produced by the cold working of metals may be accounted for in this way. The true metallic liquid possesses a much greater kinetic energy than the crystalline solid. but the amorphous state which is produced by the cold working of metals must have an even greater kinetic energy than the ordinary liquid, because of the high pressures that are necessary to keep it in that condition.

---

[1] *Zeitschrift für Electrochemie*, 1912, vol. xviii., p. 584.

[2] *Engineering*, 1913, vol. xcvi., pp. 509-511, 537-539.

[3] *Iron and Steel Inst.*, 1914, No. 1, p. 178.

It has been shown that the hardness which has been developed in metals as a result of cold working can be readily removed by heating to a moderately low temperature. This is explained by the recrystallisation of the amorphous layers. The actual temperature at which this recrystallisation is completed varies in different metals, and is also dependent upon the time of heating.

Professor G. Tammann explains the whole of the above phenomena in a somewhat different manner. He says that the hardening by cold straining is produced as a result of the formation of an increasing number of crystalline lamellæ, without any destruction of the true crystalline arrangement. Whilst the metal is being subjected to deformation energy is absorbed as a result of the formation of so many new bounding surfaces, and this reappears in the hardened metal, in the form of increased solution, pressure, etc. According to this view, a worked metal differs from an unworked, in having its crystals definitely oriented, owing to the development of cleavage lamellæ and twinning.

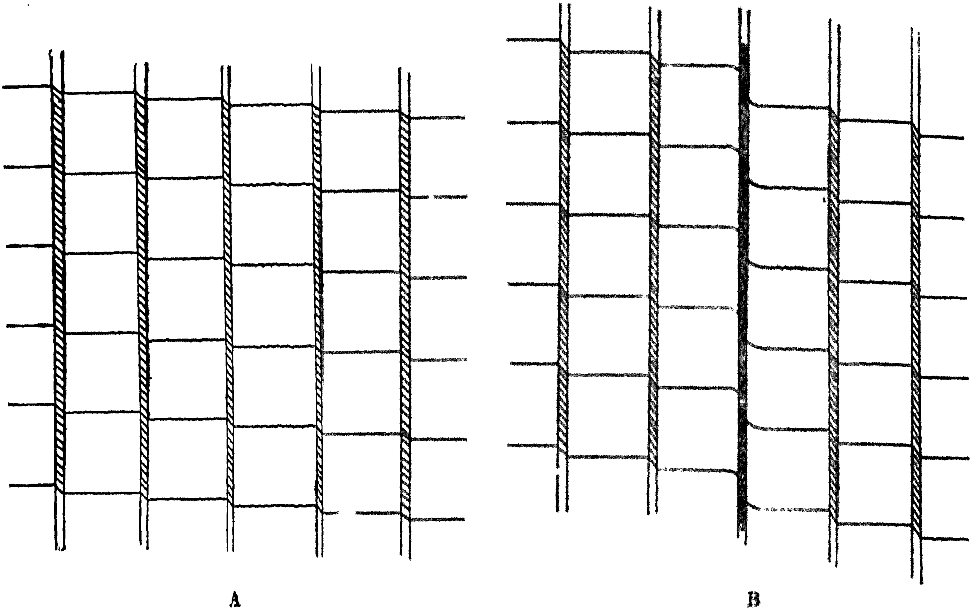


Fig. 127. (*Chappell*).

This theory has been considerably developed in an excellent paper which was recently published by Mr. C. Chappell.[1] He is of the opinion that when metals are subjected to stress the molecular or crystal units at the cleavage or gliding planes are brought into a state of high tension (Stage A, fig. 127). This corresponds with the condition which exists until the stress actually

---

[1] "The Recrystallisation of Deformed Iron," *Journ. Iron and Steel Inst.*, 1914, No. 1, p. 460.

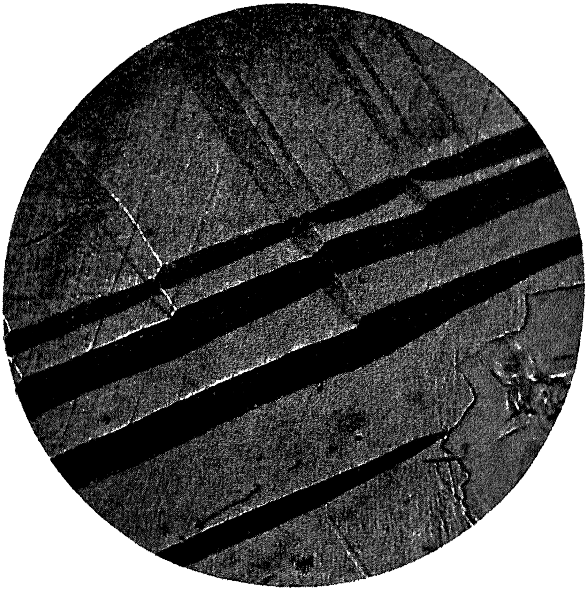


Fig. 128.—Showing Twin Crystals formed in Tin by Bending in Compression. × 1

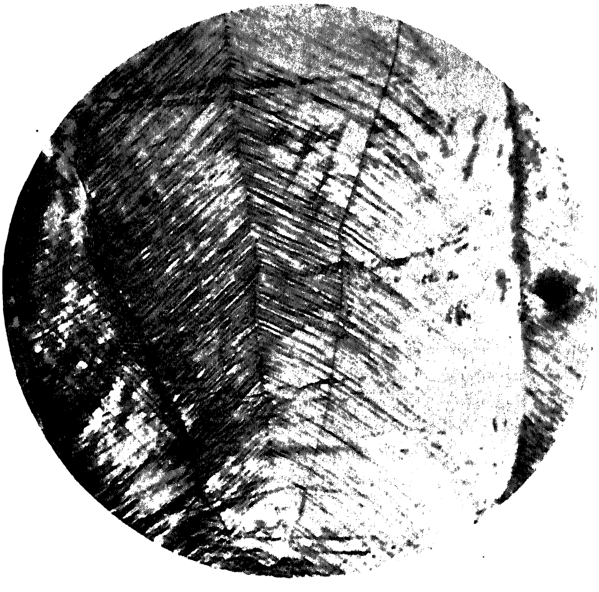


Fig. 129.—Slip Bands formed in Tin by Bending in Tension. × 150.

reaches that of the elastic limit of the material. "When, however, by further deformation along one of these planes, the tension becomes greater than the molecular cohesion, the molecular continuity is broken, and the deformation along this plane becomes permanent" (Stage B, fig. 127). This would then constitute exceedingly fine twin lamellæ. "Moreover, by the simple grinding together of these two surfaces in the course of further deformation, a layer of debris is produced between them, in just the same way as when two stones are rubbed together." He considers that this debris still retains its crystalline nature, and may be regarded as a layer of highly metacrystalline material. He quite legitimately says that the decreased density which accompanies plastic deformation may be accounted for by the fact that the debris, though still crystalline, will occupy a larger volume than when fitted together accurately in the crystalline mass, just as bricks occupy a larger volume when in an irregular heap than if built into a wall. It will be seen that this theory is in many ways similar to the amorphous theory advanced by Dr. Beilby, and supported by Dr. Rosenhain, but when it is applied to the phenomena which Mr. Chappell was considering, it certainly seems to possess some advantages. Up to the present it has not been possible to test which is really the correct view; in fact, it may be found that both are true up to a certain point, but that each has its limitations. So far as one is able to judge, it is purely a matter of opinion as to which of the two should be accepted, and it would, therefore, be unwise to make any dogmatic assertion until more conclusive evidence is available.

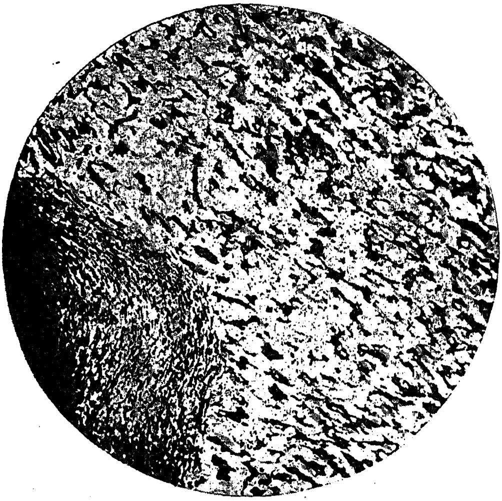


Fig. 130.—Showing Effect of Local Deformation upon the Structure of Mild Steel. × 150.

It may be of interest to note at this stage that it has been shown by Professor Carpenter and the present author[1] that the crystals of certain metals are capable of becoming twinned by direct mechanical deformation. Thus, tin, zinc, and cadmium will readily form twin crystals. The case of tin is particularly interesting, and may prove to be very important theoretically; it has been shown by the author that when this metal is bent in compression the crystals are immediately twinned (fig. 128), but when subjected to pure tensional strains only the ordinary slip bands are developed (fig. 129). These facts indicate that the plastic deformation of metals is not always accompanied by a process of pure slipping alone, but that in at least some instances fine twin lamellæ are formed. This leads one to wonder whether the ordinary cases of deformation of metals is indeed due to true slip upon the gliding planes, or whether what are now regarded as slip bands are exceedingly fine twin lamellæ far beyond the powers of the microscope.

---

[1] *Journ. Iron and Steel Inst.*, No. 1, 1914.

The effect of local deformation upon the structure of mild steel is illustrated in fig. 130.

Rapid Recrystallisation of Iron and Mild Steel after Deformation and Annealing at Certain Temperatures.

The first detailed account of the remarkable recrystallising properties of strained iron and steel was published by Dr. Stead.[1] He found that "in practically carbonless pure irons and steels of fine grain produced by forging . . . the grains increase slowly in size at 500° C., and more rapidly between 600° and 750° C., and it is possible by heating for a few hours at about 700° C. to develop granular masses of exceeding coarseness. When pure iron made coarsely granular by long heating at a dull red heat is heated between 750° and 870° C., as a rule the structure is not altered to any material extent, but as soon as the temperature rises to about 900° C. the granules again become small."

Other investigations which have a direct or indirect bearing upon this question have been published by Goerens,[2] Heyn,[3] Brunton,[4] Longmuir,[5] Charpy,[6] Le Chatelier,[7] Sauveur,[8] Robin,[9] and, finally, by Chappell,[10] in a most interesting and instructive paper.

It has been observed by a number of the above workers that this phenomenal crystallisation is dependent upon the actual amount or degree of mechanical deformation. Thus, on annealing a specimen which has been locally deformed in carrying out the Brinell ball hardness test excessive crystallisation takes place only in certain parts of the deformed area. Abnormal crystal growth does not occur if the deformation be above or below

---

[1] "The Crystalline Structure of Iron and Steel," *Journ. Iron and Steel Inst.*, 1898, No. 1, p. 145.

[2] "On the Influence of Cold Working and Annealing on the Properties of Iron and Steel," *Iron and Steel Inst.*, vol. iii., 1911, p. 320.

[3] "Die Umwandlung des Kleingefüges bei Eisen und Kupfer durch Formanderung im Kalten Zustande und darauf folgendes Ausglühen," *Zeit. des Vereines deutscher Ingenieure*, 1900, No. 1, p. 433.

[4] "The Heat Treatment of Wire," *Iron and Steel Inst.*, 1906, No. 2, p. 142.

[5] "Some Aspects of Wire Drawing," *Iron and Steel Inst.*, 1912, No. 2, p. 188.

[6] "Sur la Maladie de l'ecrouissage," *Revue de Metallurgie*, 1910, vol. vii., p. 655.

[7] "Notes de Metallographie," *Revue de Metallurgie*, vol. viii., 1911, p. 367.

[8] "Growth of Ferrite Below its Thermal Critical Point," *Proc. of the International Association of Testing Materials*, Sixth Congress, 1912, vol. ii.

[9] "Researches sur le developpement des grains des metaux par recuit apres écrouissage," *Revue de Metallurgie*, vol. x., 1913, p. 752.

[10] "The Recrystallisation of Deformed Iron," *Iron and Steel Inst.*, 1914, vol. i., p. 460.

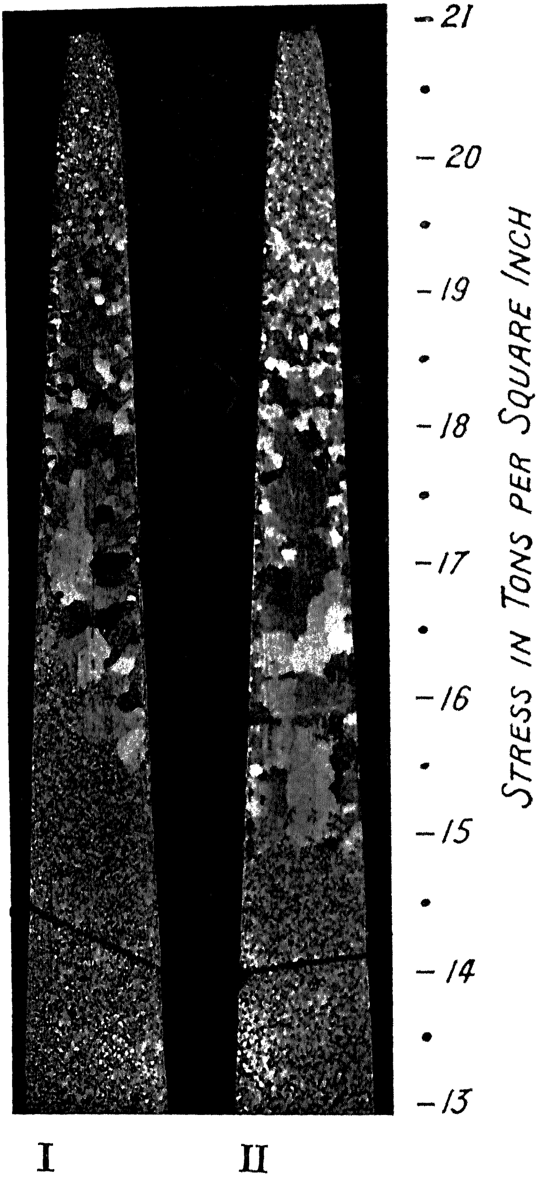


Fig. 131.—Magnified 4·75 diameters (*Chappell*).

a certain degree; in other words, there is a maximum and minimum limit of straining which will give this peculiar crystallisation. This fact is very clearly illustrated in fig. 131, which represents the structure of test bars of wrought iron that have been tested to destruction and then heated to 870° C. At both ends it will be observed that the crystals are normal in size, but the material in the middle has developed exceedingly large crystals. This phenomenal change in the size of crystals takes place on heating the specimen for only ten minutes at 870° C.

Chappell has also examined the effect of straining very pure iron whilst it is at varying temperatures, and has found that abnormally large crystals are always produced providing the temperature at which the material is deformed is not above 900° C. This is an important practical fact, and may serve to explain why it is that the so-called ingot iron can only be rolled, etc., at high temperatures—viz., above the Ar_3 critical point or 900° C. The forging of ingot iron at a red heat, but below 900° C., is always accompanied by a disintegration of the metal very similar to that which accompanies the rolling of over-oxidised steel, but no difficulty is experienced if the rolling or forging be conducted at temperatures above 900° C. This may be due to the formation of the large crystals which accompanies deformation at temperatures below 900° C. When carbon is present, as in mild steels, this phenomenal crystal growth is prevented by the presence of the second constituent—*i.e.*, the solid solution of carbide of iron in iron, which isolates the various ferrite crystals from one another.

Chappell offers two feasible explanations of the rôle of plastic deformation in promoting the union of ferrite crystals.

(*a*) If the view be adopted that identity of orientation is the only condition necessary for union of adjacent crystals, then plastic deformation may be considered to act by increasing the potential energy of the crystals, and thus enabling them to bring about this rotation of their axes parallel to each other with greater ease and rapidity on rise of temperature.

(*b*) The union of ferrite crystals may be considered analogous to the welding together of two pieces of iron, in which work is necessary to break up any separating layer of oxide or flux, and thus establish molecular contact between the two metallic surfaces. Such a view would be compatible with the idea of a cement between the crystals acting as a separating layer, the penetration of which might be regarded as being a function of the plastic deformation, after which penetration the two crystals in contact on reaching a sufficient temperature weld directly together, and not by a process of gradual transference.

Each of these theories may be used to explain the rapid growth of deformed ferrite crystals, but neither seems to take into account the absence of material growth when the deformation has been carried beyond a certain limit. This part of a deformed bar, seen in the upper section of fig. 131, seems to be more readily explained on the assumption that the material has almost completely lost its crystalline character, and that any subsequent annealing merely permits the amorphous material to recrystallise.

CHAPTER XII.

THE PROPERTIES OF COLD-DRAWN WIRE AND THE EFFECT OF ACID CLEANING.

For the many interesting technical details connected with the manufacture of iron and steel wire, reference should be made to the excellent papers dealing with this subject by J. P. Bedson,[1] J. D. Brunton,[2] and Percy Longmuir.[3]

All that is necessary here is to give a brief summary of the processes, which will enable readers more readily to appreciate some of the characteristic features and properties of the materials under discussion.

The iron or steel billets destined for the purpose are first rolled down whilst hot to wire rod of a size suitable for the subsequent drawing operations. In some works this wire rod is annealed at a red heat, above the highest recalescence point, in order to remove the stresses that have been set up during the hot rolling process. P. Longmuir says that if the rod as hot-rolled be not in a state of equilibrium as regards stresses, cold work intensifies, and to some extent "fixes," its condition, and any later heat treatment does not necessarily remove this "fixed habit." There is no doubt that this fixed habit is caused by overworking the material, which develops inside the drawn wire a continuous series of actual or incipient flaws or fractures, such as are shown in fig. 132. It is obvious that when internal defects of this kind are once produced they cannot be removed by annealing or anything short of remelting. Before passing the hot-rolled rod through the draw-bench dies, it is, therefore, necessary to see that the metal is in such a condition as to render it capable of withstanding the severe deformation of wire-drawing.

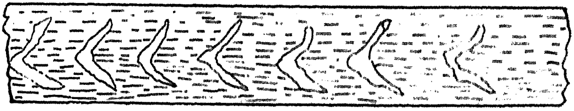


Fig. 132.

Thus, if it already retains appreciable strains as a result of the later stages of hot rolling, it is capable of withstanding proportionately less cold-drawing before becoming permanently injured. Before cold-drawing the rod, the surface oxide is removed by immersing in a tank of dilute hy chloric or sulphuric acid. It is then well washed with water completel remove the acid, and coated with a mixture of lime and water, which is allo to dry on the surface. One end of the wire is then pointed, so that suffic can be pushed through the die and firmly held by the grips. Inequal in the section of the rod are very deleterious, because they cause irregular in the cold flow of the material during drawing.

---

[1] "Iron and Steel Wire, and the Development of its Manufacture," *Journ. Iron and Steel Inst.*, 1893, No. 2, p. 77.

[2] "Wire and Wire Drawing," *Journ. of West of Scotland Iron and Steel Inst.*, 1900; and "The Heat Treatment of Wire," *Journ. of Iron and Steel Inst.*, 1906, No. 2, p. 142.

[3] "Some Aspects of Wire Drawing," *Journ. of Iron and Steel Inst.*, 1912, No 2, p. 188.

The percentage of carbon contained in steel has a marked effect upon amount of cold work it is capable of supporting without breaking. Th clearly illustrated in Table X.

TABLE X.

Original Cross Section.	Carbon.	Reduction of Area of Material drawn to Breaking Point.
Mm².	Per cent.	Per cent.
21·2	0·1	96·5
22·6	0·5	86·5
22·06	0·8	67·5

The progressive change in the mechanical properties of the various l of steel, at different stages of wire-drawing, has been carefully investig by P. Goerens,[1] and the figures given in Tables XI. to XVI. have been t from his paper, which contains so much valuable information that impossible to refer here to more than a few of the more important de No one interested in this subject should fail to make a careful study o original paper.

TABLE XI.—Wrought Iron, 0·11 per cent. Carbon.

Mechanical Treatment.	Reduction of Area in Drawing.	Tensile Strength.	Elongation.	Contract
	Per cent.	Kg. per mm.²	Per cent.	Per ce
Hot-rolled (untreated), .	. .	41·5	26·1	44·7
Subjected to 1 drawing, .	10·8	48·4	10·7	39·2
,, 2 drawings, .	25·4	56·7	6·0	32·1
,, 3 ,, .	39·8	63·5	3·5	17·5
,, 4 ,, .	43·6	(63·5)	0·5	8·2
,, 5 ,, .	48·3	(63·0)	1·5	10·9

---

[1] “On the Influence of Cold Working and Annealing on the Properties of Iro Steel,” *Journ. of Iron and Steel Inst.*, 1911, No. 111, p. 320.

TABLE XII.—ELECTRIC STEEL, 0·12 PER CENT. CARBON.

Mechanical Treatment.	Reduction of Area in Drawing.	Tensile Strength.	Elongation.	Contraction.
	Per cent.	Kg. per mm.^{2}	Per cent.	Per cent.
Hot-rolled (untreated), .	..	41·3	32·7	70·0
Subjected to 1 drawing, .	9·1	52·9	15·6	66·3
,, 2 drawings, .	14·2	56·7	13·7	65·8
,, 3 ,, .	22·6	60·0	10·2	65·8
,, 4 ,, .	28·3	65·6	6·7	52·8
,, 5 ,, .	44·3	77·2	6·0	42·2
,, 6 ,, .	70·4	84·5	6·0	30·0

TABLE XIII.—ELECTRIC STEEL, 0·27 PER CENT. CARBON.

Mechanical Treatment.	Reduction of Area in Drawing.	Tensile Strength.	Elongation.	Contraction
	Per cent.	Kg. per mm.^{2}	Per cent.	Per cent.
Hot-rolled (untreated), .	..	48·7	29·9	59·5
Subjected to 1 drawing, .	9·1	62·8	13·2	49·1
,, 2 drawings, .	15·4	68·0	9·3	43·3
,, 3 ,, .	22·6	73·0	4·5	39·2
,, 4 ,, .	28·3	74·6	4·5	35·4
,, 5 ,, .	44·3	86·4	2·9	25·2
,, 6 ,, .	70·4	96·6	3·0	22·7
,, 7 ,, .	broke	(85·0)	(0·5)	..

TABLE XIV.—OPEN HEARTH STEEL, 0·55 PER CENT. CARBON.

Mechanical Treatment.	Reduction of Area in Drawing.	Tensile Strength.	Elongation.	Contraction.
	Per cent.	Kg. per mm.^{2}	Per cent.	Per cent.
Hot-rolled (untreated), .	..	65·5	23·3	38·0
Subjected to 1 drawing, .	34·0	98·5	6·8	19·4
,, 2 drawings, .	55·0	111·3	5·9	15·3
,, 3 ,, .	62·6	119·5	6·5	14·0
,, 4 ,, .	78·6	133·4	6·0	14·1
,, 5 ,, .	86·5	142·2	6·3	13·4

TABLE XV.—Open Hearth Steel, 0·78 per cent. Carbon.

Mechanical Treatment.	Reduction of Area in Drawing.	Tensile Strength.	Elongation.	Contraction.
	Per cent.	Kg. per mm.²	Per cent.	Per cent.
Hot-rolled (untreated), .	..	81·2	19·2	36·0
Subjected to 1 drawing, .	25·4	101·4	7·6	24·2
,, 2 drawings, .	36·7	109·0	6·9	19·8
,, 3 ,, .	47·5	121·0	5·9	20·2
,, 4 ,, .	58·5	126·2	6·2	17·5
,, 5 ,, .	67·5	128·0	6·0	15·5

TABLE XVI.—Electric Steel, ·98 per cent. Carbon.

Mechanical Treatment.	Reduction of Area in Drawing.	Tensile Strength.	Elongation.	Contraction.
	Per cent.	Kg. per mm.²	Per cent.	Per cent.
Hot-rolled (untreated), .	..	103·0	6·7	7·8
Subjected to 1 drawing, .	9·1	118·0	0·9	3·0
,, 2 drawings, .	14·2	121·0	0·6	2·8
,, 3 ,, .	22·6	126·5	0·7	3·4
,, 4 ,, .	28·3	131·0	0·3	2·5
,, 5 ,, .	32·8	(127·0)	..	..

The increase in the density which is brought about by annealing cold-drawn mild steel is also shown in fig. 133. The specific gravity of the cold-rolled material is 7·806, and that of the completely annealed 7·822—that is, an increase of ·205 per cent. as a result of annealing.

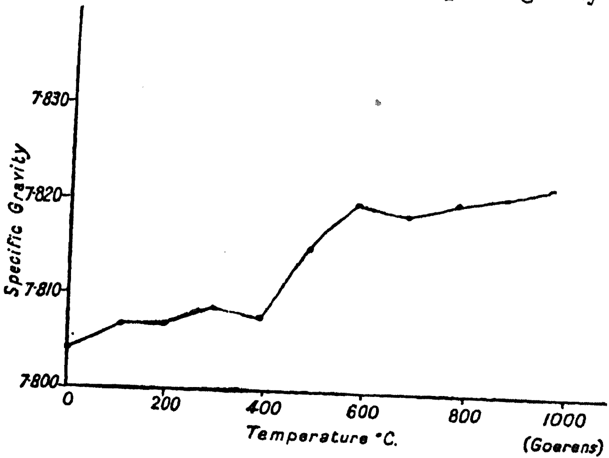


Fig. 133.

In regard to the effect of annealing temperatures upon the hardness of cold-drawn steel, Goerens concludes that after a short period of heating to 520° C. the effects of the cold-working of mild steel are almost completely removed. Several hours' heating at temperature between 495° and 500° C. only removes to a slight extent the hardness produced by cold-working. These facts are very clearly manifested in the flexibility tests which he conducted (fig. 134). This test consisted in determining how frequently a piece of the wire could be bent backwards and forwards through an angle of 180°, each bend of the wire from the vertical position to 90° and back again counting as one bend.

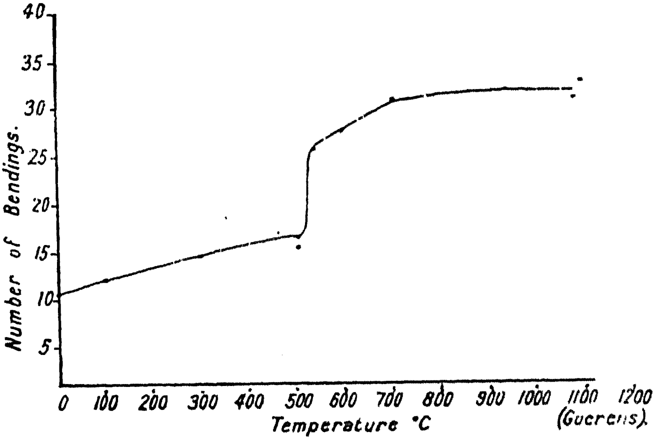


Fig. 134.

Galvanising or Coating with a Thin Film of Zinc.

Cold-drawn wire or cold-rolled sheets are frequently galvanised or covered with a thin coating of zinc for certain purposes where the materials are exposed to atmospheric conditions. After cold-drawing or rolling the iron or steel is first annealed, and then cleaned or "pickled" by dipping in dilute acid to remove all dirt and surface oxide. This cleansing operation is absolutely necessary, and must be carefully carried out in order to obtain an adherent coating of zinc. After cleaning the wire or sheet, it is passed through a bath of molten zinc, and readily takes up a coating of that metal and emerges at the opposite end through a bed of sand, which regulates the thickness of the zinc covering. In the early days of the galvanising industry the cleaning and zincing were done in two distinct stages. It was found, however, that the wire often became exceedingly brittle as a result of the action of the weak acid, which was left on the surface of the material, between the two operations. The continuous process is now in general use, and the wire passes directly from the acid bath into the molten zinc. In this way the wire or sheet is in contact with the acid only for a very brief period, and the embrittling from that cause is entirely eliminated. It has been pointed out by Mr. Bedson that the embrittling of iron and steel on cont with acid is really due to the metal absorbing a quantity of the nasc hydrogen which is generated in the pickling process. He also states t the injurious effects of the hydrogen could readily be removed by heat the metal to a temperature below that of the melting point of zinc—v 419° C. It is not known whether this heating actually removes the hydro or not, but there are good reasons for considering that it merely cause redistribution of that element which neutrallises its effects.

The data given in Table XVII. are taken from a paper by Percy Lo muir,[1] because they indicate very clearly the effects of different acids, e and also the temperatures at which the properties of the material are resto Unless otherwise stated, the time the steel was in contact with the a was just sufficient to remove the layer of oxide.

TABLE XVII.—The Effect of Acid Cleaning on Steel, as Jud by the Arnold Alternating Stress Test. Rail Steel Rol to ¾-inch Round.

Treatment.	Alternating Stress Test Reversals.
Cleaned by sand blast, ...	200
,, in pure sulphuric acid, 1·5 per cent. water, . .	58
,, ,, hydrochloric acid, 2·5 per cent. water, .	47
,, ,, acetic acid, ...	59
,, ,, commercial spirit, ...	101
,, ,, ,, ,, and blued, . . .	200
,, ,, ,, ,, and heated to 800° C., .	225
,, ,, ,, salts, and heated to 800° C., .	102
,, ,, ,, ,, and blued, . . .	190
,, ,, ,, ,, twice normal time, .	80
,, ,, ,, ,, twice normal time and blued,	140
,, ,, ,, ,, thrice normal time, .	53
,, ,, ,, ,, ,, ,, and blued,	100

The term "blued" means that the specimens were heated in a stov a temperature of from 100° to 150° C. for a period of 12 hours. Knov that the relatively rapid generation of hydrogen upon the surface of s during the pickling process will cause such remarkable brittleness, it was very surprising that P. Longmuir suggested that the hydrogen whicl produced in the ordinary atmospheric corrosion of steel may have a sin effect. He pointed out that the rust which is formed upon the surfac steel exposed to the atmosphere always contains much more sulphur t could possibly have come from the metal itself. This seems to indi that in such cases the corrosion is largely due to the presence of oxide sulphur in the air becoming concentrated in the moisture which is depos on the metallic surface. In other words, it is acid corrosion which will rise to the liberation of free hydrogen. This idea must be seriously conside because it may supply an explanation of many disconcerting failures of s Among several instances which have come before the author of the q deterioration in the properties of wire rope, one in particular is most in esting and significant, when viewed in the light of the above suggest The rope in question was a "spare," which had been kept in stock for al a year; it had been carefully wrapped up in cloth, but in a few places the covering had been disturbed and the steel exposed to the atmosphere. Although only slight rusting had occurred on the exposed parts, in all those places the material had become so brittle that the strands of wire were broken by simply uncoiling the rope.

---

[1] "Corrosion of Metals," *Iron and Steel Inst.*, No. 1, 1911, p. 163.

Action of Caustic Soda.

In a paper on the "Ageing of Mild Steel," Mr. Stromeyer [1] drew attention to an instance where the steel of a boiler in which caustic soda had been concentrated had developed pronounced signs of deterioration. He referred to an earlier instance, when it had seemed unreasonable "to suppose that a caustic liquor should in any way affect steel." His attention had, however, been forcibly drawn to the matter, and it appeared that "if the concentration of the soda liquor is allowed to proceed beyond 100° Twaddle, not only does the mild steel become brittle in quality, but tubes and plates crack and rivet heads fly off. Rivet heads even fly off in steel tanks in which cold caustic soda of over 100° Twaddle is stored. Hot caustic soda corrodes mild steel, a rod which was recently exposed to this influence being reduced in diameter at the rate of $\frac{1}{10}$ inch in fourteen days' exposure. It has been suggested that air which in this case at least had access to the liquor parts with some of its oxygen to the iron, and that an iron salt of soda, perhaps ferrate of soda, is formed, which is soluble in solutions of soda and water, but not in molten caustic soda; but until the matter has been cleared up, one should not reject the possibility that, in the presence of caustic soda and iron, water splits up the oxygen forming ferric oxide or acid, which combines with the caustic soda, whilst the hydrogen is occluded by the iron metal. This would account for the extraordinary brittleness which is imparted to mild steel vessels in which caustic soda liquor is being concentrated, more particularly as this brittleness makes its appearance, chiefly if not exclusively, in closed vessels in which air is not admitted and where corrosion, if at all active, is very slight."

Mr. J. H. Andrew [2] has made a noteworthy contribution to our knowledge of this subject. He explains the corrosion of iron by caustic soda on the assumption that there are two phases present in the metallic mass—viz., the crystalline and the amorphous cement or envelopes surrounding the various crystals. The amorphous phase, which is really the supercooled liquid, will absorb much greater quantities of hydrogen than the crystalline variety. Hence, when the iron is in contact with the caustic soda solution the atomic hydrogen which is liberated is absorbed by the amorphous layers, and as the amount of hydrogen taken into solution increases, the amorphous material becomes less and less stable. This instability naturally increases the tendency for that particular phase to crystallise, and this can only be effected by the actual growth of the pre-existing crystals. Thus, as Andrew has shown, the hydrogen causes excessively large crystals to be produced, which is accompanied by very pronounced brittleness. Even if it is found that no amorphous cement exists at the boundaries, it will only be necessary to slightly modify Andrew's explanation, and consider that the hydrogen increases what Tammann calls the solution pressure at the crystal boundaries.

---

[1] *Iron and Steel Inst.*, 1909, vol. i.

[2] "Embrittling of Iron by Caustic Soda," *Faraday Society*, vol. ix., part 3, 1914

CHAPTER XIII.

CEMENTATION AND CASE-HARDENING.

For many industrial purposes certain machine parts are required which have a very tough interior and an exceedingly hard working surface. Such parts are usually manufactured from very mild steel containing about 0·12 per cent. of carbon, and after machining to the desired shape the specimens are subjected to the cementation process, whereby the carbon content of the outside shell is raised to about 0·9 per cent. This outer surface is then hardened by quenching from a red heat (about 800° C.), a treatment which does not sensibly affect the mild steel core.

The cementation or carburising process consists in surrounding the articles with some suitable carbonaceous material contained in a tightly fitting iron box, and heating to temperatures of about 900° C.

When it is desired to keep any particular surface or part of the steel soft, for subsequent machining purposes, etc., that part is protected from the carburising elements by a coating of some inert material. Fire-clay is frequently used for this purpose, but it is very liable to crack, in which case it does not afford perfect protection. For very important work, Dr. Guillet recommends a coating of electro-deposited copper, which can be removed after hardening.

The actual time necessary to keep the steel at the carburising temperature largely depends upon (1) the thickness of the coating required, (2) the temperature of cementation, and (3) the composition of the carburising material.

The thickness of the casing is usually determined by the engineer, and varies more or less with the particular article required.

As regards the carbonising temperature, it is well known that the rate at which iron absorbs carbon at temperatures below the Ac_3 point—*i.e.*, about 915° C.—is remarkably slow. Above that temperature carbon readily enters into solution with iron, and the rate at which this occurs increases as the temperature rises. Carbon is, of course, the essential element of all carburising mixtures, but there is no doubt that the presence of other compounds, and especially of nitrogen compounds, plays a very important rôle in this process. Indeed, this is so much the case that the purer forms of carbon, such as wood charcoal, or anthracitic coal, are seldom used for commercial case-hardening. Other substances which are more effective, although more expensive, are preferred. The effect of the composition of the carburising medium upon the rate of cementation will be readily seen from the figures in Table XVIII., which are taken from a paper by G. Shaw-Scott.[1] These figures were obtained by using specimens 3 inches long and 6·5 mm. square section, which were kept at a uniform temperature of 900° C.

---

[1] *Journ. Iron and Steel Inst.*, 1907, No. 3.

TABLE XVIII.

Time of Heating.	Leather.	Wood Charcoal.	Wood Charcoal and $BaCO_3$.
2 hours, . . .	1·15 mm.	0·72 mm.	1·36 mm.
4 ,, . . .	1·58 ,,	1·07 ,,	2·20 ,,
8 ,, . . .	2·30 ,,	1·58 ,,	2·80 ,,
12 ,, . . .	2·80 ,,	1·80 ,,	3·17 ,,
16 ,, . . .	right across	the specimen.	

From the above figures giving the depth of carbon penetration in millimetres, it is clear that pure wood charcoal is not nearly so effective as leather and the mixture of wood charcoal and barium carbonate. The exact action of barium carbonate is not understood, but it has been suggested that it possesses some property which enables it to absorb nitrogen from the air, contained in the cementation box, with the formation of an effective cyanide of barium. Be that as it may, there can be no doubt that the presence of such nitrogen compounds as cyanides and ammonia bring about a very pronounced increase in the rate of cementation.

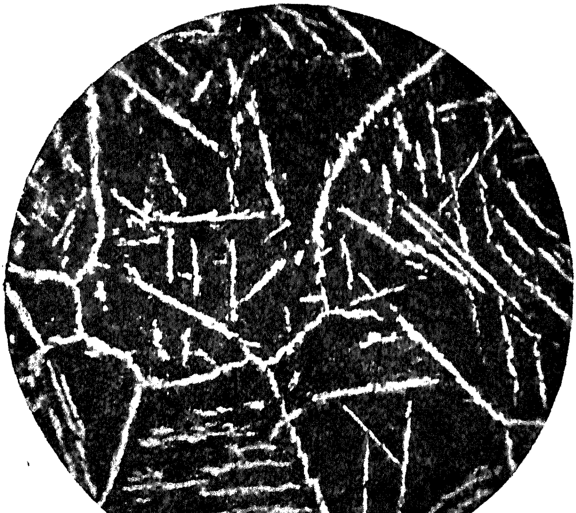


Fig. 135.—High Carbon Steel. × 150.

Cementite = White.
Pearlite = Dark.

For normal case-hardening, a "case" of approximately the same composition as the eutectoid steel—viz., 0·90 per cent. of carbon—should be obtained. With higher carbon an excess of cementite exists around the pearlitic areas (fig. 135). These boundaries constitute a source of weakness, and can only be removed or broken up by quenching from higher temperatures in the final hardening operation. Quenching from higher temperatures increases the chances of producing quenching cracks, in the hardened surface, and these are very injurious. The actual hardening operation consists in quenching the cemented specimens, from temperatures of about 800° C., either in water or in oil. If the initial steel contain only about 0·12 per cent. of carbon, this quenching has practically no effect upon the mechanical properties of the interior of the case-hardened specimens.

When rather large objects have to be treated, and a comparatively thick casing produced, the time it is necessary to keep the mass at the carburising temperature is sufficient to bring about a material coarsening of the crystalline structure, which means a deterioration in the mechanical properties of the steel. If the best possible results be aimed at, this coarse structure should be removed before hardening. A detailed account of the recommendations made by the Society of American Testing Association for the heat-treatment of case-hardened carbon steel objects is given below.

(1) When hardness of casing only is desired, lack of toughness or brittleness being unimportant, the carburised objects may be quenched by emptying the contents of the boxes into cold water or oil. Both the core and the case are then coarsely crystalline.

(2) In order to reduce the hardening stresses, and to decrease the danger of distortion and cracking in the quenching bath, the objects may be removed from the box and allowed to cool, before quenching, to a temperature slightly exceeding the critical range of the case—namely, 800° to 825° C. Both the core and the case remain coarsely crystalline.

(3) To refine the case and increase its toughness, the carburised objects should be allowed to cool slowly to below 700° C., and should then be reheated to a temperature slightly exceeding the Ac_1 change (775° to 825° C. is suitable), and quenched in water or, for greater toughness and less hardness, in oil. The objects should be removed from the quenching bath before their temperature has fallen below 100° C. This treatment refines the case, but not the core.

(4) To refine both the core and the case and increase their toughness, the objects should be allowed to cool slowly below 700° C., and should then be—

(*a*) Reheated to a temperature exceeding the critical points of the core, which will generally be from 900° to 950° C., followed by quenching in water or oil; and

(*b*) Before they have cooled below 100° C., they should be reheated to a temperature slightly exceeding the lower critical point of the case, say, to a temperature of 775° to 825° C., and again quenched in water or oil.

(5) In order to reduce the hardening stresses created by quenching, the objects, as a final treatment, may be tempered by reheating them to a temperature not exceeding 200° C.

The quenching operation frequently produced distortion of the case-hardened objects, and it is, therefore, necessary to readjust or straighten them. This trouble, which is inevitable with carbon steels, can be eliminated by using nickel steel. Dr. Guillet has pointed out (see Chapter XV.) that, by using a steel containing 0·12 per cent. of carbon and 7·0 per cent. of nickel, case-hardening can be effected simply by raising the carbon of the outside surface to 0·9 per cent., followed by slow cooling. The combined action of 0·9 per cent. of carbon and 7·0 per cent. of nickel is sufficient to keep the steel in the martensitic or hard condition, whilst, with only 0·12 per cent. of carbon in the core, that part is in the soft state.

CHAPTER XIV.

METHODS OF TESTING HARDNESS.

The property or combination of properties which are generally associated with the term "hardness" are extremely interesting, and very important both from a purely metallurgical standpoint, and from the practical engineer's point of view. It is, therefore, not surprising that large numbers of papers dealing with the many scientific and practical aspects of this subject have been published. But even now we cannot claim to have a really clear conception of the manner in which the various factors, which are believed to govern this particular property, react one upon the other, and determine the degree of hardness possessed by different metals and alloys. This somewhat unsatisfactory state of affairs is rendered much less easy to grapple with when it is remembered that there are at least four types of hardness which are usually regarded as being quite distinct from one another. These are:—(*a*) elastic hardness, (*b*) indentation hardness, (*c*) wearing hardness, and (*d*) machining hardness. Considering that the general term "hardness" is frequently used without any qualification for each of the above qualities, it is quite natural to expect that confusion will arise as to its meaning.

With regard to elastic hardness and resistance to indentation there are two methods which are universally used for estimating these two properties. These are the Brinell method and the Shore scleroscopic method. The former is a static test, in which the hardness of the metal is taken as the measure of its resistance to penetration by a hardened steel ball under a steadily applied load. In the latter the hardness is indicated by the height of rebound of a small hammer, which is allowed to drop from a fixed height, after producing a permanent, though small, indentation in the surface of the specimen under test.

Brinell Test.—The Brinell number is $\frac{P}{S} = H$. Where $P =$ the load in kilogrammes and $S =$ the superficial area of the concave surface of the indent in mm^2. As Brinell found in his early experiments the number obtained in this way is influenced by the diameter of the ball used and also by the pressure under which it is forced into the surface of the specimen. The effect is (1) for the Brinell number to increase as the size of ball decreases. and (2) to increase as the pressure which is used is raised.

Benedicks (1), who has examined Brinell's method in some detail, has considered the indentations produced from three different aspects.

1st. $\dfrac{P}{\frac{\pi d^2}{4}}$, that is, the total pressure divided by the circular area of the indent. This would appear to be the simplest expression and is that which was suggested by Auerbach (2).

2nd. $\frac{P}{S}$, S being the spherical area of the surface of contact, which is Brinell's number; and

3rd. By examining the values of (1) and (2) after multiplying them by a function of the radius of the ball.

The following data in Tables XIX. and XX. are taken from Benedicks' thesis. In Table XIX. are given the values for lead with a 6 mm. ball under loads varying from 2·0 to 25 kilos. It will be observed that under these conditions neither $\frac{P}{\frac{\pi d^2}{4}}$, nor $\frac{P}{\frac{\pi d^2}{4}}\sqrt[5]{\rho}$ are constant, thus indicating that the hardness number increases with the increase in the applied pressure.

Load.—With a 6 mm. ball under varying load.

TABLE XIX.

ρ	P	d	$\frac{P}{\frac{\pi d^2}{4}}$	$\frac{P}{\frac{\pi d^2}{4}}\sqrt[5]{\rho}$
3	2·0	0·86	3·4	4·3
3	4·0	1·08	4·4	5·45
3	6·0	1·33	4·3	5·4
3	9·0	1·58	4·6	5·7
3	12·0	1·78	4·8	6·0
3	15·0	1·98	4·9	6·1
3	20·0	2·25	5·0	6·3
3	25·0	2·45	5·3	6·6

The effect of varying the size of the ball when the pressure is kept constant is shown in Table XX., from which it will be seen that $\frac{P}{\frac{\pi d^2}{4}}$, decreases as the size of the ball increases. It will also be noted from the figures given in column 5 that a constant is obtained when the values in column 4 are multiplied by the fifth root of the radius of the ball.

TABLE XX.

ρ	P	d	$\frac{P}{\frac{\pi d^2}{4}}$	$\frac{P}{\frac{\pi d^2}{4}}\sqrt[5]{\rho}$
1·56	21·0 Kilos.	2·17	5·7	6·2
2·97	21·0	2·25	5·3	6·6
3·94	21·0	2·42	4·6	6·0
4·96	21·0	2·42	4·6	6·3
1·56	31·0	2·61	5·8	6·3
2·97	31·0	2·72	5·3	6·6
3·94	31·0	2·91	4·7	6·1
4·96	31·0	2·94	4·6	6·3

The useful application of Benedicks' correction by multiplying H by $\sqrt[5]{\rho}$, is very clearly demonstrated by the figures given in Tables XXI. and XXII. In the first set of data, Table XXI., the values are for a steel containing 1·40 per cent. of carbon examined under a load of 500 kilos.

It will be seen that $\frac{P}{\frac{\pi d^2}{4}}$, and also the ordinary Brinell figures, $\frac{P}{S}$, show quite a substantial decrease as the size of the ball increases, but when both these series of figures are multiplied by $\sqrt[5]{\rho}$, the results are practically constant and almost the same in each series.

The results in Table XXII. are for three steels containing respectively 0·10, 0·45, and 1·25 per cent. of carbon tested under a pressure of 2,000 kilos. In this instance it will be clearly seen that whilst Brinell's number, $\frac{P}{S}$, materially decreases as the ball increases, the product, $\frac{P}{S}\sqrt[5]{\rho}$ is practically constant. With these higher pressures, however, it will be observed that the product of the circular area and $\sqrt[5]{\rho}$ is certainly not constant.

Hence, as Benedicks points out, Brinell was happily inspired in choosing $\frac{P}{S}$ as the hardness number.

TABLE XXI.—1·40 PER CENT. CARBON STEEL. (LOAD, 500 KILOS).

ρ	d		$\frac{P}{\frac{\pi d^2}{4}}$	$\frac{P}{\frac{\pi d^2}{4}}\sqrt[5]{\rho}$	$\frac{P}{S}$	$\frac{P}{S}\sqrt[5]{\rho}$
1·60	1·40	1·405	323	354	306	336
1·61	1·41					
2·49	1·48	1·470	295	354	288	346
2·49	1·46					
2·99	1·495	1·505	281	350	277	344
2·99	1·515					
3·97	1·550	1·550	265	349	263	346
3·97	1·549					
5·00	1·576	1·580	255	352	253	350
5·00	1·585					
6·37	1·625	1·627	240·5	348	239	346
6·37	1·630					

Influence of Pressure.—It is clearly indicated by Brinell in his early publication that his hardness figure $\frac{P}{S}$ increases with the pressure, and this has been repeatedly verified by subsequent workers. The variations thus obtained is quite marked when the indentations that are produced are small, but they are not at all serious, and, in fact, may be regarded as negligible when the deformation corresponds with an indent of above, say, 3·5 millimetres. A curve which is typical for all metals when $\frac{P}{S}$ is plotted against

TABLE XXII.—LOAD, 2,000 KILOS.

Percentage Carbon.	ρ	d	$\frac{P}{\frac{\pi d^2}{4}}$	$\frac{P}{\frac{\pi d^2}{4}} \sqrt[5]{\rho}$	$\frac{P}{S}$	$\frac{P}{S} \sqrt[5]{\rho}$
0·10	2·50	—	133	160	115	138
0·10	3·75	4·60	120	157	107	139
0·10	5·00	4·90	106	146	99	137
0·10	7·50	5·10	98	146	95	142
0·45	2·50	—	245	294	220	264
0·45	2·75	3·40	220	287	208	271
0·45	5·00	3·50	208	287	201	276
0·45	7·50	3·75	181	271	178	266
1·25	2·50	—	369	443	345	414
1·25	3·75	2·80	325	423	315	410
1·25	5·00	2·85	314	433	306	422
1·25	7·50	3 05	274	410	272	407

P is shown in Fig. 136. It will be readily understood that the load above which $\frac{P}{S}$ = constant varies from metal to metal being greater as the hardness of the metal increases. Many investigators are of the opinion that the change of $\frac{P}{S}$ with the load is due to the increase in the hardness of the metal produced by plastic deformation. This does not seem to be the correct explanation, (1) because it applies to lead, which does not appear to be hardened by cold work, and (2) the effect is much more pronounced in the

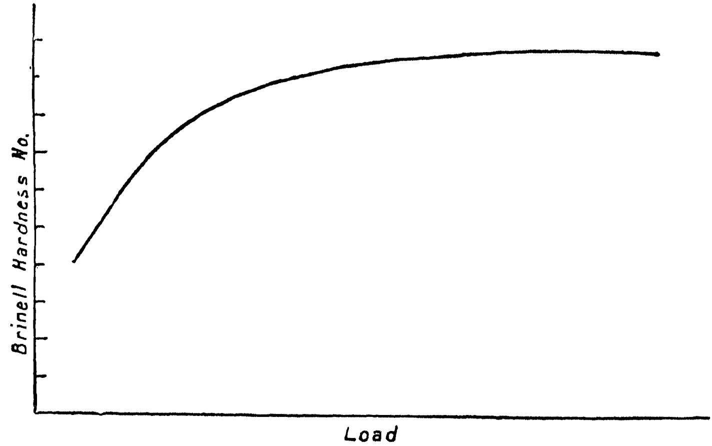


Fig. 136.

case of completely hardened steel than any other metal or alloy, and since such a metal is incapable of undergoing plastic deformation it follows that its hardness cannot be increased in that way. The observed discrepancies are most likely due to the change in the geometric shape of the indent, which is, of course, more serious for small than for large indents. Whatever may be the real cause there is no disputing the fact that there is a certain minimum load which increases with the hardness of the metal tested, below which the values are low and above which they are virtually constant. In this connection the figures given in Table XXIII. are rather significant, for they broadly indicate the minimum load which should be used in order to obtain a satisfactory Brinell figure. For very hard materials, such as hardened steels, the pressure should be something of the order of 5,000 kilos. With such hard metals it is necessary to point out that the results are influenced by an unavoidable distortion of the ball itself. Hitherto it has not been possible to make a satisfactory correction for the change in shape of the ball, but an extremely useful investigation in this direction has been made and recently published by Shore.[1]

TABLE XXIII.

Description of Sample.	Brinell Hardness Numbers.					
	Load in Kg.					
	500	1,000	1,500	2,000	2,500	3,000
Aluminium,	19	20	17	—	—	—
Copper,	79	83	82	81	80	80
Duralumin,	108	125	121	125	124	126
Mild Steel,	109	121	127	128	130	121
Nickel-Chromium Steel, Air Hardened,	175	200	207	214	224	221
Annealed High-Speed Tool Steel,	157	198	207	214	211	217
Valve Steel,	194	218	231	242	244	248
Medium Carbon Steel,	219	238	259	257	259	268
Nickel-Chromium Steel, Oil Hardened,	264	359	390	418	427	444
Hardened High-Speed Tool Steel,	—	—	472	570	548	600

Ludwik Test.—Turning to the question of the change in the geometric shape of the Brinell indents, it is interesting to note that Ludwik[2] overcomes this defect by using a right-angled cone instead of a ball. When such a cone is used the radius and depth of the indentations are always equal, and there is no change in the geometric form of the indents. Theoretically it might be claimed that this method of testing hardness is better than the Brinell ball test, but there is the insuperable practical difficulty of preserving the shape of the cone when testing hard metals. Since it is for the higher ranges of hardness where improvements in the methods of testing are more urgently required, the Ludwik test is not likely to come into general use.

---

[1] *Iron and Steel Institute*, vol. II., 1918.

[2] *Baumateriallenkunde* xii., *jahrgang*, 1907, p. 147.

TABLE XXIV.

Diameter of Impression with 10 mm. ball, Area of Impression, and Maximum Pressure in Kilogrammes per Square Millimetre.

Dia.	Area.	$\frac{5000}{A}$	$\frac{3000}{A}$	$\frac{1000}{A}$	$\frac{500}{A}$	$\frac{200}{A}$
1·50	1·8095	2770	1660	551	277	111
1·55	1·8975	2640	1582	528	264	105
1·60	2·0232	2480	1487	495	248	99·0
1·65	2·1866	2290	1373	458	229	91·5
1·70	2·2871	2180	1310	437	218	87·5
1·75	2·4378	2055	1236	411	206	82·0
1·80	2·5761	1940	1164	388	194	77·5
1·85	2·7112	1848	1108	368	185	73·8
1·90	2·8620	1750	1048	350	175	69·9
1.95	3·0159	1660	995	332	166	62·2
2·00	3·1762	1577	946	316	158	61·0
2·05	3·3427	1498	898	298	150	59·8
2·10	3·5029	1430	867	286	143	57·0
2·15	3·6757	1361	817	273	136	54·0
2·20	3·8485	1304	782	261	130	52·0
2·25	4·0275	1242	744	248	124	50·0
2·30	4·2097	1189	713	238	119	48·0
2·35	4·3982	1139	683	227	114	46·0
2·40	4·5930	1090	652	218	109	44·0
2·45	4·7885	1045	627	209	105	42·0
2·50	4·9889	1000	600	200	100	40·0
2·55	5·1931	963	578	193	96	39·0
2·60	5·4036	925	555	185	93	37·0
2·65	5·6188	889	532	178	89	36·0
2·70	5·8340	855	512	171	86	34·0
2·75	6·0586	827	495	166	83	33·0
2·80	6·2832	798	477	159	80	32·0
2·85	6.5172	767	460	153	77	31·0
2·90	6·7513	741	444	148	74	30·0
2·95	6·9696	718	430	144	73	29·0
3·00	7·1880	696	418	140	70	28·0
3·05	7·4629	670	402	134	67	27·0
3·10	7·7378	645	387	129	65	26·0
3·15	8·0001	625	375	125	63	25·0
3·20	8·2624	606	364	121	61	24·0
3·25	8·5310	587	351	117	59	23·5
3·30	8·7996	569	340	114	57	23·0
3·35	9·0792	551	332	111	55	22·0
3·40	9·3588	535	321	107	54	21·4
3·45	9·6478	518	311	104	52	20·7
3·50	9·9369	502	302	101	50	20·2
3·55	10·2353	488	293	98	49	19·6
3·60	10·5338	476	286	95	48	19·0
3·65	10·8416	462	277	92	46	18·5
3·70	11·1495	448	269	90	45	18·0
3·75	11·4495	436	262	88	44	17·5
3·80	11·7496	425	255	85	43	17·0

TABLE XXIV.—*Continued.*

Dia.	Area.	$\frac{5000}{A}$	$\frac{3000}{A}$	$\frac{1000}{A}$	$\frac{500}{A}$	$\frac{200}{A}$
3·85	12·0051	414	248	83	41	16·5
3·90	12·4407	402	241	81	40	16·0
3·95	12·7785	392	235	78	39	15·6
4·00	13·1162	382	228	76	38	15·2
4·05	13·4712	372	223	75	37	14·9
4·10	13·8262	362	217	73	36	14·5
4·15	14·1749	353	212	71	35	14·1
4·20	14·5236	345	207	69	34·5	13·8
4·25	14·8943	336	202	67	33·6	13·4
4 30	15·2650	326	196	65	32·6	13·1
4·35	15·6451	319	192	64	32·0	12·8
4·40	16·0253	312	187	63	31·2	12·5
4·45	16·4148	304	183	61	30·4	12·2
4·50	16·8044	297	179	60	29·7	12·0
4·55	17·2065	291	174	58	29·1	11·6
4·60	17·6087	284	170	57	28·4	11·4
4·65	18·0186	278	166	56	27·8	11·1
4·70	18·4286	272	163	54	27·2	10·9
4·75	18·8527	265	159	53	26·5	10·6
4·80	19·2768	259	156	52	25·9	10·4
4·85	19·7135	254	153	51	25·4	10·1
4·90	20·1502	249	149	50	24·9	9·9
4·95	20·5978	244	146	49	24·4	9·7
5·00	21·0455	238	143	48	23·8	9·5
5·05	21·5042	233	140	46·5	23·3	9·3
5·10	21·9629	228	137	45·5	22·8	9·1
5·15	22·4357	223	134	44·5	22·3	8·9
5·20	22·9085	218	131	44	21·8	8·7
5·25	23·3939	215	128	43	21·5	8·6
5·30	23·8793	210	126	42	21·0	8·4
5·35	24·3694	206	124	41	20·6	8·2
5·40	24·8720	201	121	40	20·1	8·0
5·45	25·3778	197	118	39·5	19·7	7·9
5·50	25·8931	193	116	39	19·3	7·7
5·55	26·4114	190	114	28	19·0	7·6
5·60	26·9392	186	112	37	18·6	7·4
5·65	27·4733	182	109	36·5	18·2	7·3
4·70	28·0168	178	107	35·7	17·8	7·1
5·75	28·5634	175	105	35·0	17·5	7·0
5·80	29·1163	172	103	34·4	17·2	6·9
5·85	29·6818	169	101	33·8	16·9	6·75
5·90	30·2536	166	99	33·0	16·6	6·6
5.95	30·8316	162	97	32·5	16·2	6·5
6·00	31·4160	159	95	32·0	15·9	6·4
6·05	32·0066	156	94	31·0	15·6	6·25
6·10	32·6098	153	92	30·6	15·3	6·15
6·15	33·2130	151	90	30·0	15·1	6·0
6·20	33·8350	148	89	29·6	14·8	5·9
6·25	34·4602	145	87	29·0	14·5	5·8
6·30	35·0634	143	86	28·5	14·3	5·7
6·35	35·7325	140	84	28·0	14·0	5·6
6·40	36·3828	138	82	27·5	13·8	5·5

TABLE XXIV.—*Continued.*

Dia.	Area.	$\frac{5000}{A}$	$\frac{3000}{A}$	$\frac{1000}{A}$	$\frac{500}{A}$	$\frac{200}{A}$
6·45	37·0426	135	81	27·0	13·5	5·4
6·50	37·7086	133	80	26·5	13·3	5·3
6·55	38·3872	131	79	26·0	13·1	5.2
6·60	39·0720	128	77	25·5	12·8	5·1
6·65	39·7632	126	76	25.2	12·6	5·0
6·70	40·4700	124	74	24·7	12·4	4·95
6·75	41·1832	122	73	24·4	12·2	4·87
6·80	41·9058	119	71·5	23·8	11·9	4·8
6·85	42·6409	117	70	23·5	11·7	4·7
6·90	43·3855	115	69	23·0	11·5	4·6
6·95	44·1394	113	68	23·0	11·3	4·5
7·00	44·9028	111	67	22·0	11·1	4·4

Influence of Time.—It is now generally recognised that the time during which the pressure is maintained in making an indentation test has an appreciable influence upon the results obtained. Broadly speaking, the effect in this connection varies with the hardness of the metal under test. Although this fact is accepted, the quantitative influence of time has not been thoroughly examined, but with the object of neutralising its effect it is the practice to maintain the maximum pressure for a standard time—namely, 30 seconds.

When we consider that it is possible to obtain a constant value by the somewhat arbitrary method of applying any load above a certain minimum, as in Brinell's method, we are almost tempted to conclude that we are dealing with a fundamental physical property of metals and not with a group of such unrelated properties. This we may regard as the viscosity of the material, and regard metals in the solid state as comparable with liquids of very high viscosity. Table XXIV. contains a list of indents and corresponding areas in mm.^{2} along with the Brinell hardness numbers.

Scleroscope Method.—This method of testing hardness, which is exceedingly useful, is based upon an entirely different principle from that just considered. It may roughly be described as being dependent upon the resistance to penetration under a dynamic stress, and partly upon the elastic properties of the metal. It should be clearly understood that both these factors take part in the test, and that under ordinary conditions their relative influence is not the same when samples of different hardness are being examined. The reason for this is, that the energy of impact is the same in all tests, and consequently the amount of deformation—that is, the work done on the specimen—varies with the hardness of the material; therefore the energy of rebound does not depend alone upon the elasticity of the metal, for it is influenced by the varying amounts of energy used in producing indents of different sizes. It follows from this that a straight-line relationship between the values obtained by the scleroscope on the one hand and those by the Brinell on the other cannot be expected unless some correction is made to allow for the varying energy that is absorbed in the latter test. If, however, a correction of this kind could be introduced there are good reasons for thinking that there would be a very close relationship between the elastic rebound and the Brinell values.

Dynamic Indentation Test.—Many years ago a French investigator, Lieut.-Col. Martell, conducted an extensive and important investigation on the indentations which are produced in metals under dynamic stresses. He proved that when using three different strikers having the form of quadrangular pyramids, the volume of the indent was directly proportional to the total energy of the blow. In other words, $\frac{E}{V}$ = constant, which is known as Martell's hardness number. With an instrument such as is shown in Fig. 137, which was used by the author, plastic deformations with a 10 mm. ball under a dynamic stress can be made.

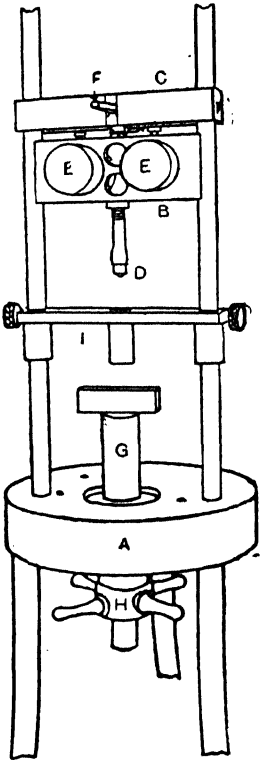


Fig. 137.—Impact Device for transmitting a known amount of energy through a hardened 10 mm. ball to surfaces under test.

This consists of a heavy base A, which is supported by three legs that are firmly screwed into it. On the upper side of the base are tightly fixed two upright rods of steel which act as guides for the weight B which slides very loosely between them. The beam or cross-piece C serves to support the weight and regulate the height from which it is allowed to fall. This beam can slide up and down on the guides. Its position can be accurately adjusted by means of two balls in spring sockets engaging in grooves exactly one inch apart, on the inner sides of the guides. The highest position of the beam permits the weight to fall 21 inches measured from the lowest part of the ball, fixed at D, to the surface of the specimen. As shown in Fig. 137 the weight was exactly 3·5 lbs., but by removing the two cylinders EE of duralumin the weight was 1·75 lbs. If, instead of duralumin, two steel cylinders were used, the total weight was 7 lbs. Hence with this simple arrangement it was possible to arrange for any degree of impact energy between 1¾ to 147 inch-lbs. The weight was released from its hanging position by pressing the handle F. Care was always taken to keep the guides well smeared with vaseline to allow the weight perfect freedom to fall, with the minimum amount of friction. That the friction was exceedingly small and insufficient to interfere with the value of the results is manifest from the fact that practically the same indentations were produced even when the weight was dropped from different heights, providing the same

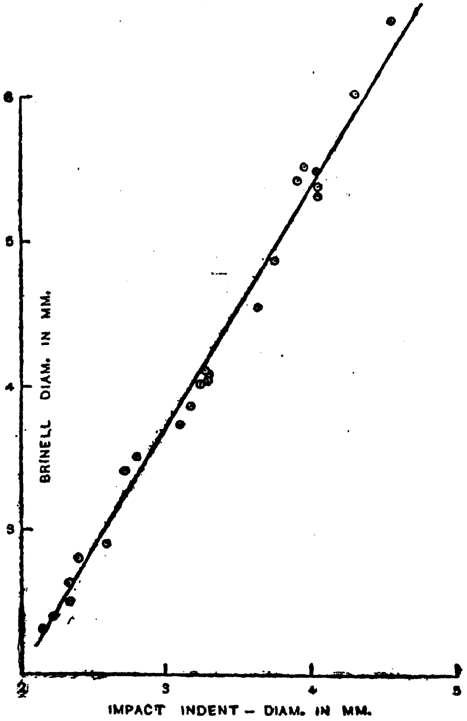


Fig. 138.—Brinell indents with load of 3,000 kg., and impact indents 63 inch-lbs.

impact energy was applied; for example, the same results were ob
with a weight of 3½ lbs. falling 20 inches as for a 7-lb. weight falling 10

Since the height from which the weight fell was determined by th
position of the grooves, the exact distance of the fall when specimens of v
thickness were being tested had to be regulated by other means. Th
done by adjusting the height of the dummy G, on which the specimen
by means of the screw H. Specimens were not allowed to rest loosely
dummy, because energy might possibly have been dissipated in thi
The samples were, therefore, rigidly held down by means of the ho
by sliding it on the guides and tightly screwing it on the specimen.
the weight is released, the striker on the lower side passes freely t
a hole in the holder and hits the specimen. Before making any exper

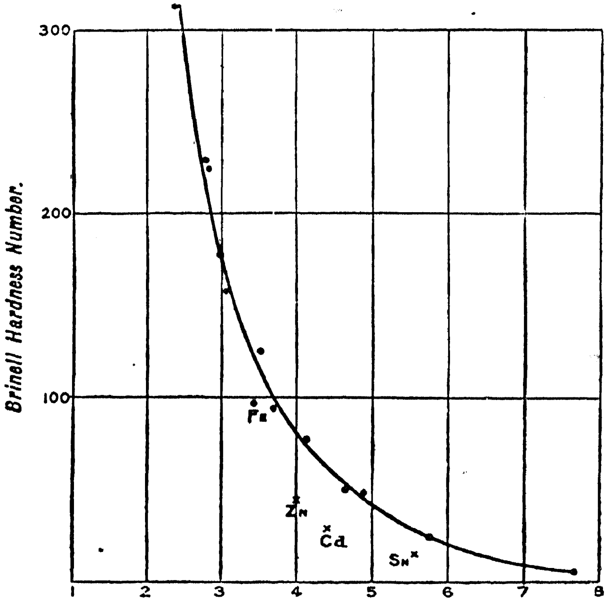


Fig 139.—Diameter of indent produced by impact of 35 inch-lbs.

the apparatus was carefully placed, so as to ensure that the guides we
perfectly vertical position, on a thickly concreted ground floor. The i
ment was in such a position during all the experiments which have been

When the diameters of the indents produced with this instrum
metals of varying hardness are plotted against the corresponding dia
made under a static load, Fig. 138, it will be seen that there is a st
line relationship between them.

If the same dynamic indents are plotted against Brinell numbers, a
such as shown in Fig. 139 is obtained. The equation for this cu
$H = \frac{7,455}{d^3}$, where H is the Brinell number and d is the diameter of the
produced by impact. There are certain anomalies to which attention

be drawn; they are the four metals—iron, cadmium, zinc, and tin. In these instances it will be noticed that the observations fall well off the main curve in such a manner as to indicate that it is relatively less easy to produce an indent under dynamic stress in these metals than in others. This must not be interpreted as meaning that with these abnormal metals a greater amount of energy is absorbed when tested by dynamic means than when tested statically; all that it indicates is that those particular elements show a relatively higher resilience under impact, and consequently give a greater rebound than would be expected when the results for other metals are taken into account. Why this should be is not known with any certainty; but the author has observed that this abnormal behaviour is associated with a special kind of deformation. The difference is this, when iron, zinc, cadmium, and tin are quickly strained, their crystals become prolifically twinned, but this does not appear to take place when they are slowly strained. So far as can be detected other metals do not possess this particular property. As regards the dimensions of the indents produced, the author has found, and Mr Batson has independently confirmed, that Martell's law $\frac{E}{V}$ = constant

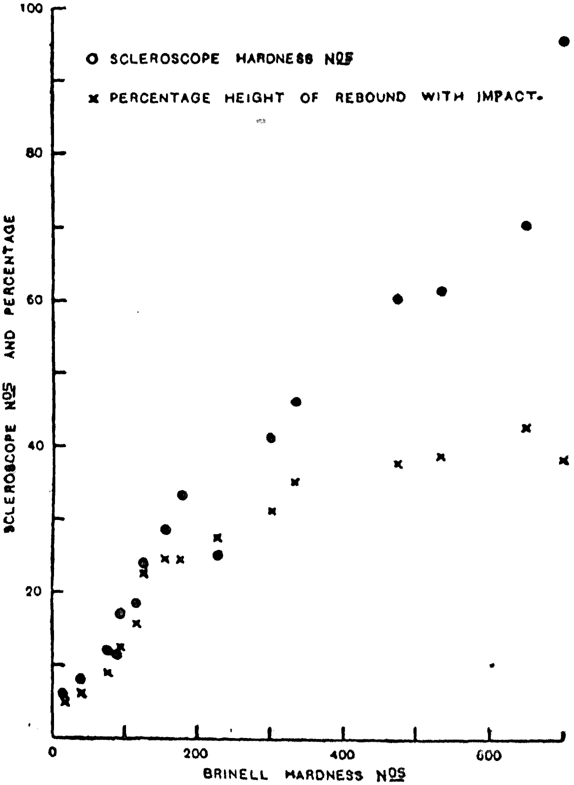


Fig. 140.—Comparison of Scleroscope Hardness Nos. with heights of rebound using new impact instrument.

is almost, if not absolutely, correct when hemispherical strikers are used. It is, therefore, an easy matter to calculate from the volume of an indent made in any metal with a known impact exactly what amount of energy would be required to give an indent of a standard size.

Dynamic Indentations and Elastic Rebound.

As previously intimated, the principle of the Shore scleroscope is that the height of rebound of the small hammer is proportional to the elastic properties of the metal tested. The inventor does not claim that this instrument measures the same kind of hardness as the Brinell method, but it would seem that the difference is not nearly so marked as would at first sight appear. Indeed, it is highly probable that, if the height of fall of the hammer could be adjusted so as to give the same size of indentation in all tests, the rebound would be directly proportional to the Brinell hardness number. Although the available data is insufficient to enable us to formulate a really definite conclusion in this respect, the results obtained by Batson and by the author indicate that the above view is substantially correct. For example, if the data obtained with the instrument, Fig. 137, and plotted in Fig. 140, are reconsidered in the light of Martell's law, see Fig. 141, it will be noted that there is a straight-line relationship between the total energy of impact required to produce a standard indent and the energy of rebound. Since the amount of work done in making a standard indent is the same, and this must bear a direct relation to the ideal Brinell number, it follows that, under favourable conditions, the Brinell value and elastic rebound must be reflexes of each other.

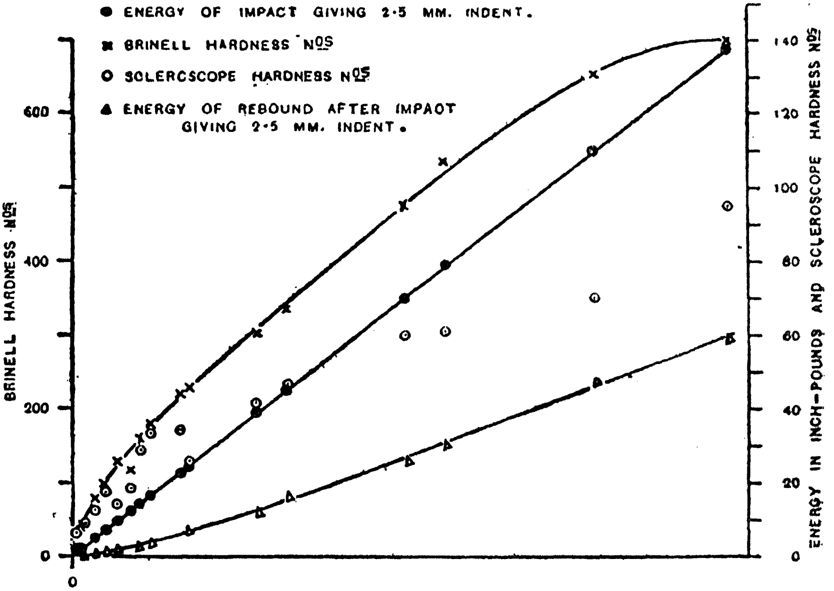


Fig. 141.—Comparison of the Brinell, Scleroscope, and Impact Indent Hardness Scales.

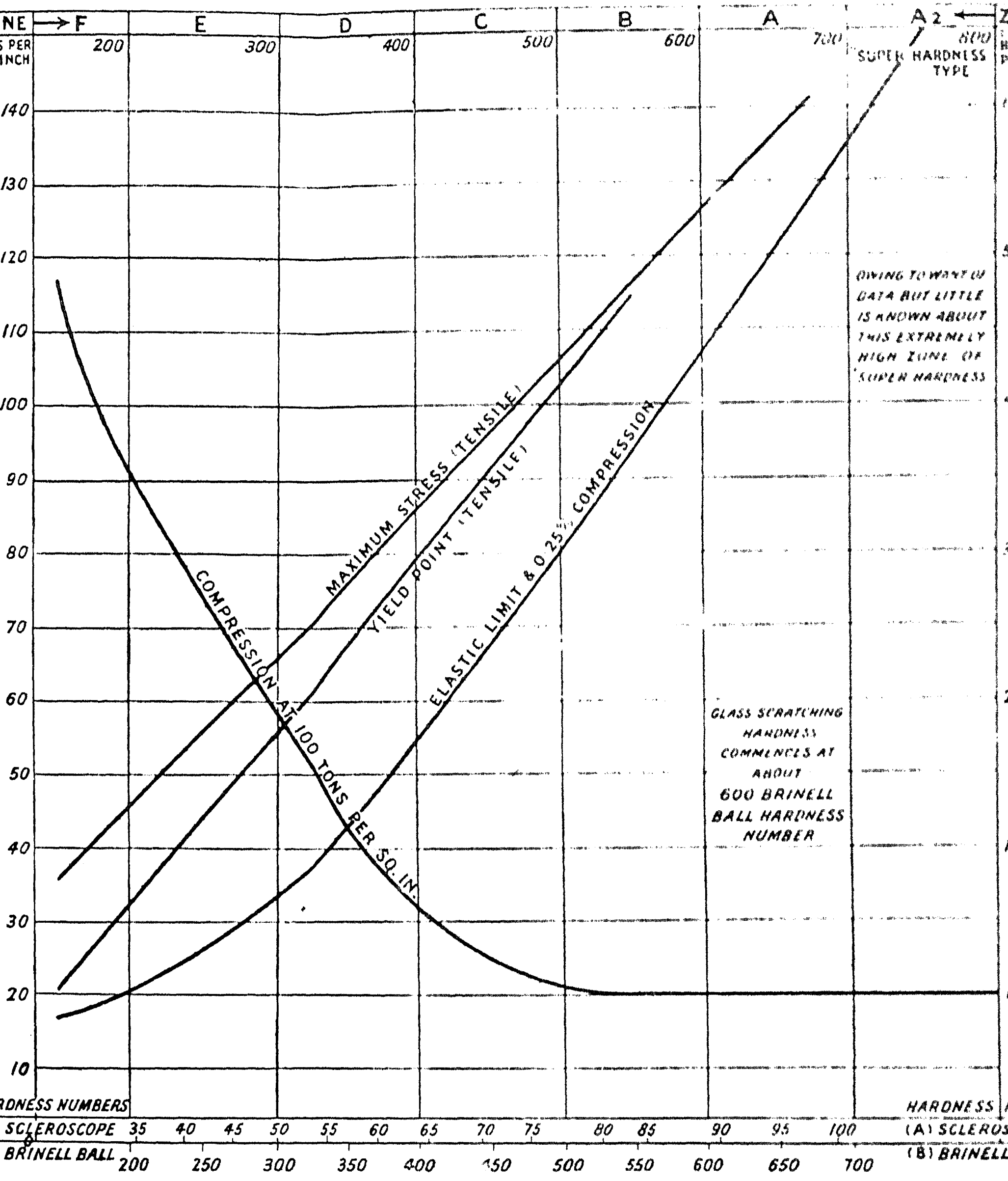


Fig. 143.—Diagram showing comparison of Brinell Ball and Scleroscope Hardness numbers wit compression strength, also yield point and tenacity of steel varying from the softest to the harde "super" hardness types.

This Diagram has been prepared by Sir Robert Hadfield from the data of Table XXV.

not more than would be anticipated from experimental error. There is a slight tendency for the results of samples possessing medium ultimate stresses to fall off the line a little more than the average for the others. The general agreement is, however, so good as to warrant the conclusion that there is a direct relationship between hardness and tensile strength which holds for steels, and may probably be applied to many, if not all, other metals and alloys which have been mechanically worked after casting and are capable of plastic deformation.

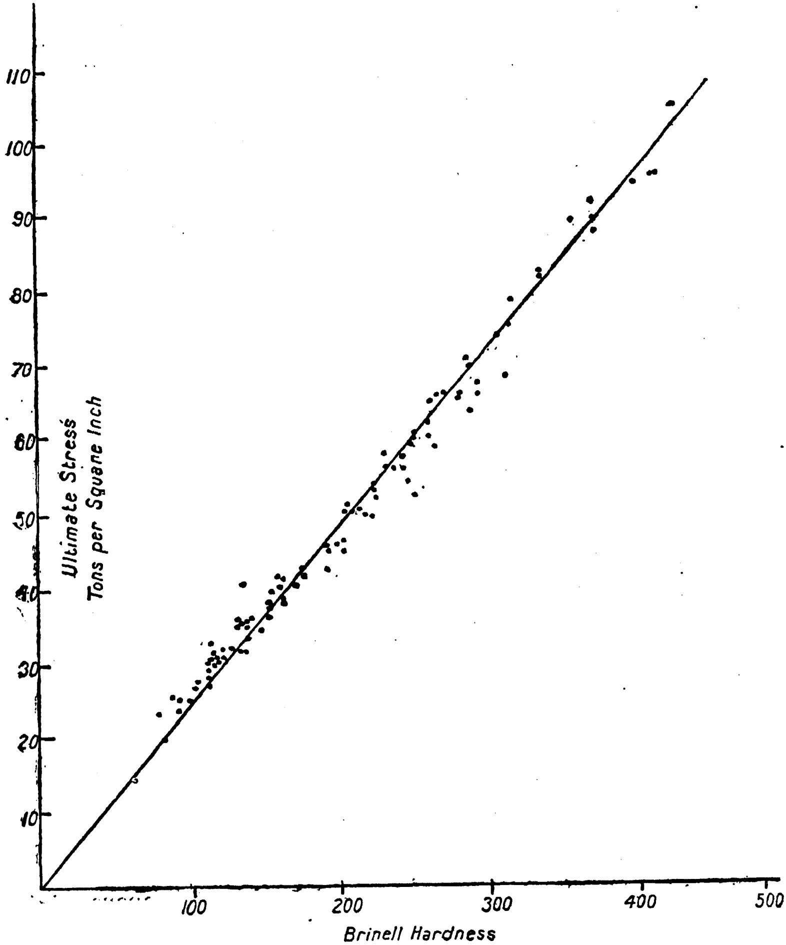


Fig. 142.

A very interesting diagram, Fig. 143, showing the relations between hardness and other mechanical properties has been constructed by Sir Robert Hadfield from the data published in the paper by Shore already quoted.

Molecular Attraction and Hardness.

The tendency amongst physical metallurgists is to regard the hardness of metals as being due to the attraction which exists between their molecules. This attraction, which is usually described as intrinsic pressure or internal cohesion, is considered to be identical with the corresponding attractive forces which are known to exist in gases.

In Boyle's law for gases, which is written $p\,v = \mathrm{R\,T}$, no account is taken of molecular attraction. Of course it is well known that ordinary gases do not strictly obey this law, and it is recognised that the deviations are due to the forces of attraction which exist between the molecules. To allow for this, van der Waals has modified Boyle's expression and writes—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{R\,T}.$$

$\frac{a}{v^2}$ is termed the internal pressure, and b is the limiting volume at which the molecules of a gas are actually in contact with each other. The above equation has been used by Traube and applied to a consideration of the solid state. He has calculated the internal pressure for a number of solids, and found that the modulus of elasticity and internal pressure run parallel with each other. He also compared the internal pressures with hardness values, but was not satisfied with the results, and attributed the disparities to the influence of impurities on the results he had for the hardness of metals. The author has plotted Traube's calculated values for the internal cohesion against the Brinell hardnesses recently obtained for the corresponding metals, Fig. 144, and, whilst it cannot be claimed that the agreement is perfectly satis-

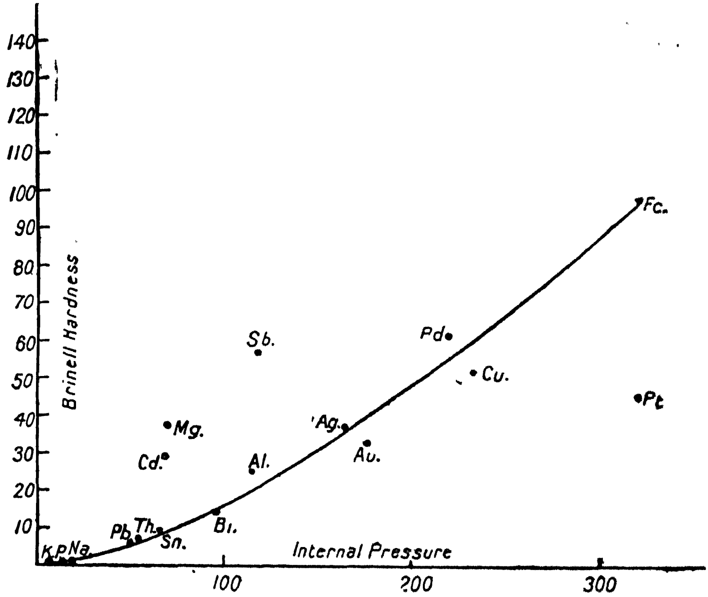
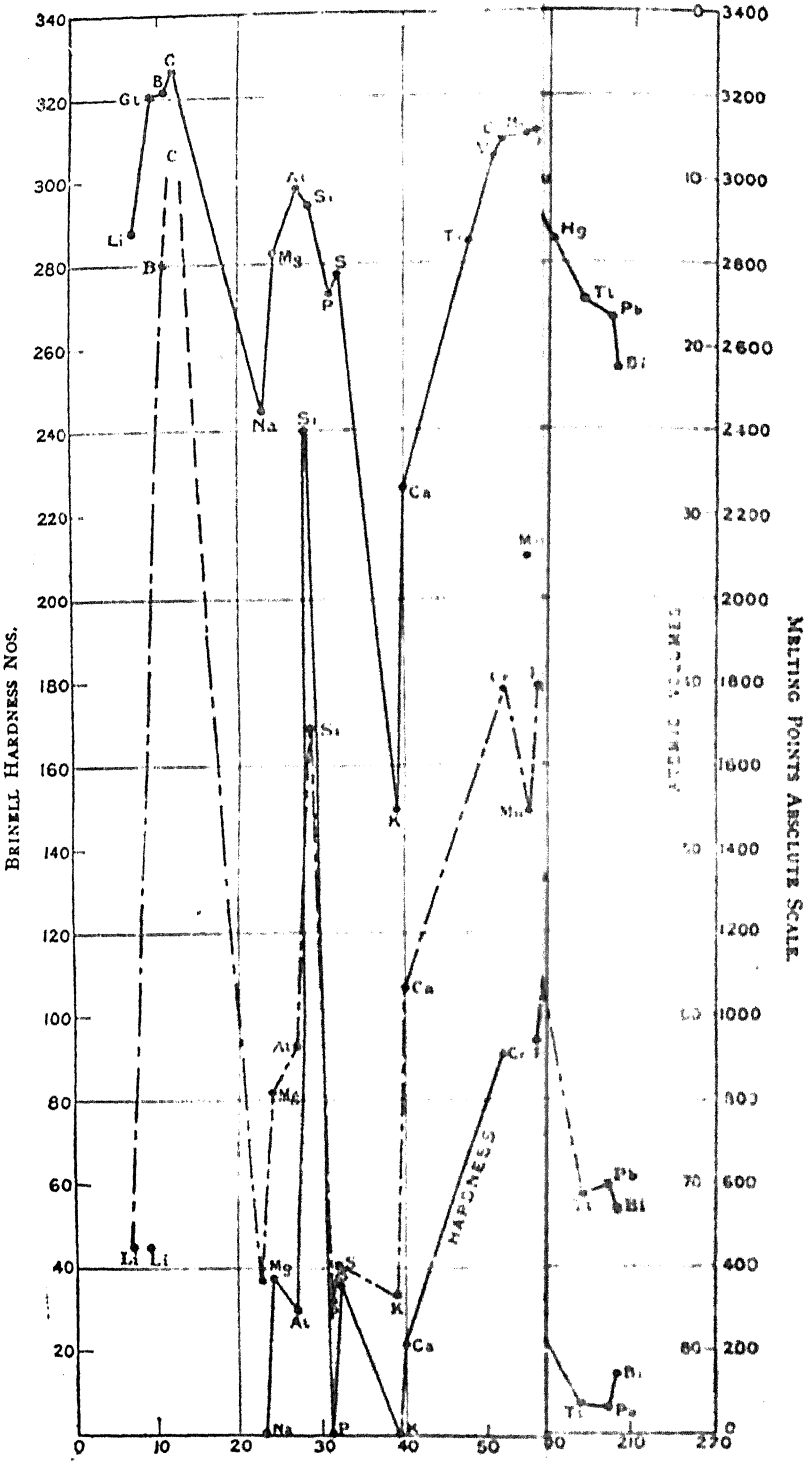


Fig. 144.

To *face p.* 161.]


BRINELL HARDNESS NOS.
MELTING POINTS ABSOLUTE SCALE.
ATOMIC VOLUMES
HARDNESS
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
270
Li
Gl
B
C
C
B
Na
Mg
Al
Si
P
S
K
Ca
Ti
Cr
Mn
Hg
Tl
Pb
Bi
Si
Si
Ca
Cr
Mn
Pb
Bi
Li
Li
Mg
Al
Al
Mg
Na
P
S
K
K
Ca
Cr
Tl
Pb
Bi

factory, the discrepancies may, apart from the question of impurities, be due to two factors which van der Waals' equation of state does not take into account.

These are, first, the possibility of a metal undergoing a complete rearrangement of the distribution of its molecules in space, and, second, the case of a metal which may be mon-atomic over one range of temperature becoming di-atomic over another range. Either of these changes would undoubtedly cause an alteration in the hardness of a metal, but no provision is made for them in van der Waals' equation.

Hence, the calculated values for internal cohesion cannot be expected to agree with the experimentally determined hardness for a metal coming under either of these categories. In this connection it may be interesting to note that, in the case of antimony, which gives a more widely different calculated value for internal cohesion than would be anticipated from its Brinell hardness, Bragg[1] has shown that its molecules are di-atomic, whereas in copper, where the theoretical and calculated values are much closer, the molecule is mon-atomic. Ludwig[2] has shown that antimony is one of the metals which rapidly loses its hardness as the temperature is raised to a certain point, after which the fall becomes much less rapid.

Many attempts have, from time to time, been made to give an explanation of the different hardnesses of pure metals. In 1873 Bottone[3] advanced the view that hardness varied directly as the number of atoms per unit volume. This view has since been supported by other workers. In column 1, Table XXV., are given the atomic volumes of a number of solid elements, and the corresponding Brinell numbers are arranged in column 2. Both these series of figures are plotted in Fig. 145 against the respective atomic weights. It will be seen that both factors follow some kind of periodic function of the atomic weight. Richards[4] has shown that when the electric properties, coefficient of expansion, and compressibility are plotted in this way they show the same kind of periodic variation. The view that hardness varies with the atomic volume may be quite correct if the determinations were made at temperatures immediately below the melting points, but an examination of the data given in Table XXV. strongly suggests that atomic volume cannot possibly be the only factor which determines the degree of hardness possessed by a metal. For example, sodium and calcium, which have very nearly the same atomic volumes, have quite different hardnesses, and, indeed, the latter, which has the greater atomic volume of the two, is much the harder; again, iridium, with a higher atomic volume than iron, chromium, or copper, is considerably harder than any of those elements. Therefore, whilst it may be admitted that atomic volume plays an important rôle as regards the hardness of pure metals, it is certainly not the only governing factor, and it is necessary to enquire what other physical properties are concerned. After a rough examination of other constants, and the well known fact that hardness is materially affected by heat, we are immediately

---

[1] May Lecture, Inst. of Metals, 1916, No. 2.

[2] *Zeitschrift für Physikalische Chemie*, vol. xci., 1916, p. 232.

[3] Bottone, *Chemical News*, 1873, p. 215.

[4] *Transactions of Chemical Society*, 1911, vol. xcix.; *Journ. of American Chemical Society* (36), pp. 2417-2439; and *Journ. of Chemical Society*, 1915, vol. ii., pp. 16 and 518

TABLE XXV.

Element.	Atomic Volume.	Brinell Hardness.	$\frac{Tm - t}{V \times E}$
Sodium,	23·7	·07	·29
Magnesium,	14·3	38·30	10·3
Aluminium,	10·5	24·7	15·1
Silicon,	11·4	240·0	89·3
Phosphorus,	17·2	·63	·12
Potassium,	47·0	·04	·09
Iron,	7·1	97·0	97·0
Nickel,	6·7	144·0	85·0
Cobalt,	6·8	86·0	99·9
Copper,	7·1	53·0	49·3
Zinc,	9·5	45·5	8·4
Arsenic,	13·3	147·0	62·4
Rhodium,	8·5	156·0	148·0
Palladium,	9·3	61·0	71·6
Silver,	10·3	37·0	26·8
Cadmium,	13·0	29·0	5·49
Indium,	16·1	1·0	1·28
Tin,	16·2	9·0	3·5
Antimony,	17·9	58·0	17·4
Iridium,	8·6	217·0	177·4
Platinum,	9·1	44·0	116·0
Gold,	10·2	33·0	39·7
Thallium,	17·2	7·3	3·2
Lead,	18·2	6·9	3·3
Bismuth,	21·2	14·0	5·3

led to the conclusion that the distance from the melting point of the temperature at which determinations are made must be given careful attention. Of course, the most satisfactory way of considering this side of the question would be to make the hardness tests of the different metals when they are in corresponding states—*i.e.*, at equi-distant temperatures from their respective melting points on the absolute temperature scale. Unfortunately there is as yet insufficient data along these lines, and in the absence of reliable quantitative data it may be useful to consider the results for ordinary atmospheric temperature. Considering only atomic volume and temperature so far as is possible the most satisfactory agreement between what may be provisionally regarded as theoretical values, and those obtained experimentally, is found by assuming that hardness is proportional to the distance from the melting point, and inversely proportional to the atomic volume, or $\frac{Tm_1 - t}{V} = H$, where Tm is the absolute melting point, and t is the temperature at which the test is made. The figures obtained in this way are very much more nearly proportional to the determined hardness than is the case when atomic volumes alone are taken into account. For the most part they are roughly equal to or a multiple of the Brinell numbers, but in the case of such elements as sodium, potassium, phosphorus, and indium, which have low melting points, the calculated figures are far too high. To bring these elements into the general scheme it is necessary to consider at least one other variable. The factor which next appears to demand attention is the change in atomic volume, with temperature. Assuming that the coefficient of expansion is really a linear function of temperature, we can calculate the atomic volume for any desired temperature. The alteration in atomic volume with change of temperature is, however, so small as to make it quite evident that if its effect is of the same order as previously considered, its influence upon the above equation would be practically negligible. If, however, we suppose that this change of volume acts on the hardness more or less independently of the real volume, and state that its influence is inversely proportional to the temperature, then its effect would be brought out much more prominently. The expression would then be $\frac{T_m - t}{V \times C \text{ of } E} = H$, or, hardness would, in accordance with this expression, vary in proportion as the distance from the melting point, but in the inverse direction as the product of the atomic volume and coefficient of expansion. With this modification the calculated figures for phosphorus, sodium, potassium, and indium very closely agree with the experimental values. It will, however, be noted that there are still irregularities (compare column 3 with column 2, Table XXV.), but they can scarcely be regarded as serious when it is remembered, first, that the tests have not been made at corresponding temperatures; second, it has been necessary for the time being to assume that the coefficient of expansion is a linear function of temperature, and, third, it has not been possible to take account of any internal molecular transformation that might occur in some of the elements at certain definite temperatures. If we take only one of these—namely, the third—and examine it in the light of the results obtained by Ludwik for the change of hardness with temperature for antimony, zinc, and cadmium, it would seem that if it were not for some internal molecular rearrangement taking place well above 15° C., the difference between the Brinell hardness of these elements and the values obtained by means of the equation would be very small. For if the upper sections of Ludwik's[1] hardness curves for these three elements are extended down to the ordinary temperature, and the transformations which take place are thus tentatively eliminated, the values are then approximately the same as those obtained from the equation. Of course, this equation cannot be regarded as perfectly satisfactory, but it appears to embrace the more fundamental factors governing the resistance to penetration of pure metals.

---

[1] *Zeitschrift für Physikalische Chemie*, vol. xci., 1916, p. 232.

CHAPTER XV.

THEORIES OF HARDENING STEELS.

THE fact that steel can be hardened simply by heating to a bright red heat and quenching in a relatively cool liquid medium, such as water, has been well known and utilised for ages. It is to this particular property of steel that civilisation owes, directly or indirectly, so many of the advances that have been made.

In view of the great importance of this property, it is not surprising that many attempts have been made to explain theoretically how it is brought about and what is its precise cause. When, likewise, the complexity of the problem is taken into account, it is not very remarkable that the conclusions arrived at have, in many respects, been widely different. The various theories that have from time to time been advanced have been subjected to severe criticism, and although the controversy has developed along lines which have sometimes seemed to confuse the issue, it has stimulated further investigation, and the publication of valuable data, and thus served a useful purpose.

Even now it would be unwise to dogmatise, because it is quite possible that some important fact still awaits discovery, which will necessitate a modification of any conclusion now drawn from the most reliable data at present available.

Briefly, it is known that hardening is in some way connected with the effect of quenching upon the Ar_1 critical point which occurs at 700° C. in carbon steels. Further, it is acknowledged that the degree of hardening is practically proportional to the magnitude of the Ar_1 change, and, therefore, the maximum effect is produced with about 0·9 per cent. of carbon. Until comparatively recently the theories that were formulated could more or less be classed in two groups—viz., those which attribute the hardening to the presence of a particular allotropic modification of the iron, and those in which it is considered that the hardening is associated with a certain condition of the carbon as it exists in the quenched steel. In recent years there has been a decided tendency to consider the question in a much broader light.

The allotropic theory was first put forward by Osmond [1] in his classical research on "The Critical Points of Iron and Steel," but since that publication the interpretation of the facts upon which his theory rests, and even the theory itself, have been modified in some rather important respects. Originally Osmond was unable to decide whether the critical points Ar_3 and Ar_2 were totally distinct and independent of each other, or whether the Ar_2 point was the lower limit of the Ar_3 retarded by the presence of small quantities of carbon. Provisionally, he asserted that iron below Ar_2 possesses the molecular form *α*, and above Ar_3 the allotropic form *β*. At temperatures between those two points, when they are distinct, he considered that the metal consisted of a mixture of the two varieties *α* and *β*. He also gave figures illustrating how the position of the recalescence is lowered when the cooling of a steel containing about 0·9 per cent. of carbon is accelerated.

---

[1] *Journ. Iron and Steel Inst.*, 1890, No. 1.

Cooling.	Duration of Cooling between 705° C. and 678° C.	Hard Steel, Ar_1 Change.	
		Cooling arrested at	Temp. rises to
Slow in tube, . . .	49 seconds	671° C.	675° C.
Ordinary in tube, . .	20 „	670° C.	680° C.
Rapid in air, . . .	not determined	642° C.	651° C.
Very rapid in water, . .	„	absent	absent

As is shown by these figures, when the rate of cooling is fairly rapid, the changes produced during slow cooling are not produced on quenching. Osmond's conclusions were as follows :—"Hardened steel is a steel in which the iron and carbon have preserved more or less completely in the cold the condition which it possessed at high temperatures. The heat of the change that has not been effected remains disposable in the metal, and may be termed the latent heat of hardening. We conclude that hardened steel owes its properties principally to the presence of *β*-iron, which is hard and brittle by itself at the ordinary temperature. Carbon in the state of hardening carbon maintains iron in the *β* condition during slow cooling up to a temperature which is in inverse proportion to the amount of carbon contained in the metal. . . . The influence of carbon is of the same character as that of the rate of cooling, and both combine to produce the final result. The rate of cooling alone is not sufficient under ordinary conditions in which hardening is effected to maintain an appreciable fraction of the iron in the *β* condition. But as, under the same condition, it is easy to maintain the carbon in the state of hardening carbon, and as the hardening carbon imparts stability to *β*-iron, it is evident in what manner *β*-iron may be successfully preserved up to the ordinary temperature by the aid of carbon. The more rapid the cooling the more incomplete are the changes and the harder is the hardened metal."

It should be remembered that at that period, and for some time later, the *β* theory, as it is called, referred to the iron when at temperatures above the Ar_3 point as being in the *β* condition. That theory, as it was then known, was entirely independent of the condition of the iron when at temperatures between Ar_3 and Ar_2 points. At a later period, however, it was considered by Osmond, Roberts-Austen, and others who took the side of the allotropists, that the Ar_2 point was quite distinct from the Ar_3 critical point, and they came to the conclusion that the Ar_2 also corresponded with an allotropic change in the iron. From that time onward the *β* theory, as applied to the hardening of steels, retained the same name, but really became a different theory. Thus the range of temperature between the Ar_3 and Ar_2 became known as that in which the iron existed in the *β* state ; and what was previously known as *β*-iron (above the Ar_3 change) was afterwards spoken of as γ-iron. These alterations in the theory are of fundamental importance, particularly when the details of the case are considered. In the early stages of the theory, allotropists definitely considered that iron when in the β, which afterwards was known as γ-form, above the Ar_3 point, was hard and brittle of itself at the ordinary temperature, but subsequently they asserted that γ-iron was really soft under all conditions of its existence—*i.e.*, whether in a stable or unstable condition.

The hardening of steel by quenching was then attributed to the iron as it existed between the Ar_3 and Ar_2 points, which was first regarded as a mixture of α- and γ-iron, but later became known as β-iron. In 1893 Metcalf and Langley[1] concisely expressed the views of the "carbonist" theory of hardening. In this theory no special point is made of the fact that iron can exist in different allotropic forms. Their statement was to the effect that hardening is due to the enforced solution of the carbon in iron by sudden cooling, the hardness being a direct function of the rapidity of cooling. Hardening is accompanied by great internal stresses. The molecular strains set up produce hardening in a similar manner to that of *cold working*. Carbon alters the molecular aggregation, and the resulting strained grouping is brought about within certain temperature limits.

The controversy upon this question dates from the time of Roberts-Austen's first report to the Alloys Research Committee,[2] when Arnold and Hadfield opposed Osmond's theory, which was supported by the author of the report. Since that date the discussion has proceeded at very frequent intervals, and has been taken up by almost all metallographists, until it has become practically impossible to refer in detail to every publication. In justice to those who have interested themselves in this matter, it should, however, be remembered that, whether their contributions have been constructive or otherwise, they have served a useful purpose, and in some degree assisted in building up a sound theoretical explanation of the phenomena now under review. At the present time there are good grounds for thinking that only very slight differences of opinion exist, and even those are not of fundamental importance.

There are undoubtedly some reasons for considering that iron in the β condition (that is, when at temperatures between the Ar_3 and Ar_2 critical points) is somewhat harder than α-iron at a temperature just below the Ar_2 point.[3] That alone, however, is not sufficient proof, and is indeed only a favourable circumstance in support of the view that quenched steels owe their increased hardness to β-iron. For the β-iron theory as applied to the hardening properties of steel, it is, above everything else, necessary to prove that β-iron exists in quenched steels, or to establish upon scientific grounds that that variety of iron can reasonably be expected to exist therein.

This necessity is not confined to any particular steel or group of steels, but extends throughout the whole range, and especially to those containing about 0·9 per cent. of carbon, as they possess the power of hardening in the highest degree. It is from this particular aspect of the problem that the allotropic theory should first be judged.

In order satisfactorily to ascertain whether β-iron can exist in a quenched steel, it is necessary to consider the physical changes through which steels pass on cooling, and the precise effect of carbon upon the allotropic inversion $\gamma \rightleftarrows \beta$ and $\beta \rightleftarrows \alpha$ that occur in pure iron. In discussing the constitutional changes that occur in carbon steels (Chapter IV.), it was shown that the addition of carbon to iron progressively lowers the Ar_3 change, and when 0·45 per cent. of carbon is present, the Ar_3 change is coincident with, or to be more correct, commences at the same temperature as the Ar_2 change in pure iron. A steel containing about 0·20 per cent. of carbon on cooling from about 950° C. (at which it is a homogeneous solid solution of carbon in γ-iron) to 840° C., begins to deposit from solution a certain amount of iron which is in the β condition. As this β-iron can hold little or no carbon in solution, the solid solution from which it was deposited becomes relatively richer in carbon, from whence it follows that the temperature of the mass must fall somewhat before any more β-iron can be deposited from what may be termed the secondary solution. In steels, therefore, this transformation from the γ solid solution is a progressive one; it is not completed at one temperature, but occurs within a range. This gradual formation of β-iron proceeds with falling temperature, and the remaining γ solid solution becomes constantly relatively richer in carbon, until the temperature of the line *b c*, fig. 146, is reached, when the composition of the solid solution corresponds with the point *c*. At this temperature—viz., 760° C.—the β-iron behaves in precisely the same manner in steels as it would in pure wrought iron, and changes bodily into α-iron. That being the case, at the temperature of the line *b c*

---

[1] *Trans. Amer. Soc. Civil Engs.*, vol. xxvii., p. 382.

[2] *Proc. Inst. Mech. Engs.*, 1893, p. 543.

[3] Rosenhain and Humfrey, *Journ. Iron and Steel Inst.*, No. 1, 1913.

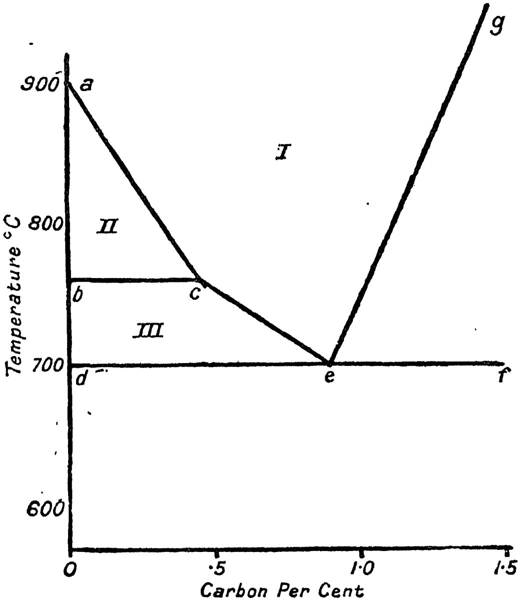


Fig. 146.

there will be three phases or constituents co-existing—namely, pure β-iro α-iron, and the γ solid solution of the composition represented by the point

Under these conditions there is what in physico-chemical terms is kno as no degree of freedom—that is, the three phases can exist together on at that particular temperature. From the fact that β-iron changes in α at the temperature of the line *b c*, it is clear that β-iron cannot exist as stable phase below that line, and the iron which subsequently separat from the γ solid solution must be in the α condition. The composition the solution then alters in the direction of the line *c e*, until it contains 0·89 p cent. of carbon at the temperature *d e f*, when the γ-iron changes bodi into α with the immediate separation of carbon as carbide of iron. It wi therefore, be readily seen that at no stage in the cooling of steels containi more than 0·45 per cent. of carbon does the β variety of iron enter in their constitution.

From the diagram (fig. 146) it is possible to predict the phase or phas —*i.e.*, the physico-chemical constitution—of any carbon steel within the limi of temperature indicated, and also the condition it would be in after perfe "ideal" quenching from any particular temperature. For example, steels so quenched from within the area I will consist of a homogeneo solid solution of carbide of iron in γ-iron. Steels containing up to 0·45 p cent. of carbon when quenched from temperatures inside the area II wou consist of the γ solid solution + β-iron. Steels containing up to 0·89 p cent. of carbon, when quenched from temperatures inside III, would consi of the γ solution + α-iron. All steels, if quenched from below *d e f*, wou consist of α-iron + carbide of iron. It is, therefore, evident that the variety of iron can exist on cooling only in those steels which contain le than 0·45 per cent. of carbon. β-iron does not enter into the constituti of those steels containing more carbon when they are slowly cooled, a there are no scientific reasons for supposing that it does even as a me transition product, when they are rapidly cooled by quenching. This co clusion, so far as it affects the β theory, is not influenced in the least degr by modifying the physical interpretation of the thermal transformati Ar_2 of pure iron. Whether the Ar_2 be merely the end or the lower limit the Ar_3 change, as Osmond originally considered possible, and as Benedic has again recently suggested, is a matter that has no direct bearing upon th particular question. Whatever the physical condition possessed by ir when at temperatures between the Ar_3 and Ar_2, that particular conditi does not, for the reasons stated above, enter into the question of the co stitution of steels with more than 0·45 per cent. of carbon.

If it be assumed, or at some future time found, that β-iron will dissol some carbon, it would make no fundamental difference to these conclusion The only difference such a discovery would make would be of a qualitati nature—viz., the temperature of the line *b c* (fig. 146) would be a little lowe It must, however, be remembered that for physico-chemical reasons t $\gamma \rightleftarrows \beta$ inversion cannot be lowered to such an extent as to be coincide with the Ar_1 or carbide change point, since there would then be four phas in equilibrium at the eutectoid point—namely, α, β, and the γ solid solutio along with carbide of iron, Fe_3C.

From this, it is therefore evident that there are very strong theoretic reasons for considering that β-iron should not be regarded as the cause of hardening. This is, so far as we can judge from our present knowledge of the subject, the only conclusion to arrive at, and it follows that the β-iron theory, as applied in this connection (which attributes the hardness of quenched steels to the presence in them of β-iron—*i.e.*, the form in which it exists in wrought iron when between the Ar_3 and Ar_2 points) cannot be logically supported by known scientific facts or laws.

In regard to the influence on hardening of the two remaining forms of iron, α and γ, one only, γ, need be seriously considered. α-iron may be dismissed, because it is known to be relatively soft at all temperatures at which it can exist above 0° C., and further, it has never been suggested that this form of iron really enters into the question. The third form of γ-iron never exists in the pure state in steels. Hence, at the present time, it is perfectly legitimate to say that neither α, β, or γ iron can, *as such*, be the cause of the hardness that occurs when carbon steels are quenched from above the critical points.

It is, however, necessary to determine how much, if anything, depends upon the fact that iron is capable of existing in different physical conditions. In the α form iron is not hard enough to be used by engineers for cutting purposes, while there is no reason for supposing that β-iron can exist in hardened steels. There can, therefore, be very little doubt that in some way hardening is due to the fact that γ-iron will hold carbide of iron in solution, and that under ordinary conditions of slow cooling that solution decomposes into α-iron and carbide of iron with the evolution of a considerable amount of heat. Although this generalisation, so far as it goes, is quite satisfactory, and is practically accepted by all metallographists, it is clearly not sufficient. At this stage it should be mentioned that the true solution of this question, whatever it may ultimately prove to be, in regard to ordinary carbon steels, must also form the foundation of the theory of hardening tool steels in general, and, consequently, must be consistent with the ascertainable physical data of those steels which contain elements other than iron and carbon.

An attempt to carry the above generalisation a step further was made by the author [1] some years ago, and is summarised as follows :—

1st. The hardness of carbon-steel tools is due to the retention, by quenching, of the solid solution of carbide of iron in iron.

2nd. Whilst this property depends upon the fact that iron can exist in the γ state—that is, dissolved carbon—it is none the less dependent upon the fact that this solution decomposes with slow rates of cooling into α-iron and carbide of iron, and that some energy must be absorbed in the specimen during the quenching process, in order to overcome the tendency for this Ar_1 inversion to take place. This energy is brought to bear in two ways—(*a*) by the sudden contraction of the outer envelope of the specimen, and (*b*) by an internal molecular contraction of the mass, which is related with the solution or osmotic pressure of the dissolved carbide.

It was pointed out in the context that these conclusions have the advantage of being applicable to alloys which contain no iron, but which are capable of being hardened in the same way as steel.

According to this explanation, it follows that the degree of hardness produced by quenching any carbon steel will depend upon the velocity and thermal magnitude of the suppressed inversion, or, in other words, with the amount of *energy it is necessary to absorb*, in preventing the inversion from taking place.

---

[1] *Iron and Steel Inst.*, vol. ii., 1910.

In this way the fact, which was first demonstrated by Osmond, that the so-called austenitic areas of quenched carbon steels are slightly softer than the martensitic areas in the same specimen can be satisfactorily explained. For, as can be readily seen from the lines *a*, *c*, *e*, *g* in fig. 146, the osmotic or solution pressure, the intensity of which they graphically indicate, increases as the percentage of carbon increases from 0·0 to 0·89, and then rapidly decreases as the amount of carbon is raised to about 2·0 per cent. It should perhaps be mentioned here that as the osmotic pressure of solution increases the freezing point of a liquid is lowered, as is also the temperature at which a solid solution deposits one of its constituents. Hence the maximum osmotic pressure in liquid solutions is found in the mixture corresponding with the eutectic composition, and in the analogous or eutectoid proportions in solid solutions.

With regard to the velocity and thermal magnitude of the critical points, it is well known from cooling curve data that the maximum effect, in both these directions, is also found in the eutectoid steel containing 0·89 per cent. of carbon. Thus, in steels containing less than 0·89 of carbon the thermal changes are spread over a wider range of temperature, and the same applies to those steels which contain more than 0·89 of carbon, with the addition that in the latter instance the thermal effect of the separation of the excess cementite is very weak, and can scarcely be detected pyrometrically. It is, therefore, evident that the maximum combined physical effect of iron and carbon is met with in steels containing 0·89 per cent. of carbon, and since there is no doubt that the hardening is directly connected with the osmotic pressure, and thermal critical points, etc., it is natural that the maximum degree of hardness should be obtained by quenching steels of that composition, and that the so-called austenite should be a little softer than martensite.

Our knowledge of this subject has been materially widened by the publication of a very important paper by Grenet.[1] Following entirely different lines of thought, Grenet had arrived at almost exactly the same conclusions as those cited in the author's paper. There are, however, one or two differences that are of fundamental importance, and should be very carefully studied. Grenet considers that quenching as compared with slow cooling may act as follows :—

(*a*) By changing the nature of the constituents and, notably, by preventing wholly or partly the transformation on cooling. In this case, which is rare, so far—that is, as steels are concerned—the quenched state and annealed state are physico-chemically different states, and their properties cannot be foreseen. It may, however, be said that in the few instances in which such quenching is known the quenched state is often softer than the annealed state

(*b*) Quenching may also act by lowering the temperature of the transformation on cooling. In this, which is the most usual case, the quenched metal is always harder than the annealed metal.

---

[1] *Journ. Iron and Steel Inst.*, No. 2, 1911.

Grenet considers that the increased hardness produced by quenching steels, and alloys in general, is due, not to the suppression of an inversion, but to the drawing out or lowering of the temperature at which it takes place. Thus, he states that :—" An alloy is the harder in proportion as the transformation which has given birth to its constituents at the time has taken place at a lower temperature, has been more rapid, and as the maximum temperature reached since the last transformation has been at a lower temperature, and has been maintained for a shorter period of time." . . . "We are thus led to the conclusion that hardness produced by quenching is due solely to the fineness of the structure."

These conclusions are both interesting and valuable; in some respects they constitute a definite step in the right direction, but in others they appear to be based upon certain assumptions that are doubtful, and are also at variance with certain accepted data which have a direct bearing upon the question.

The statement that, by rapidly quenching carbon steels, the Ar_1 inversion is not suppressed is quite contrary to actual experimental facts, for, as was originally shown by Osmond, cooling curves of steel specimens taken during the quenching period showed no signs of heat evolutions so long as the quenching was properly conducted, and the steel was thereby hardened. The same investigator also demonstrated by two other methods that the inversion or evolution of heat is suppressed by quenching.

(1) By dissolving in equal volumes of a saturated solution of the double chloride of copper and ammonia, equal weights (1·5 grammes) of different steels, successively annealed and hardened, and measuring the quantity of heat liberated in each case by the reaction

$$2CuCl_2 + Fe = 2CuCl + FeCl_2.$$

The rises in temperature, after all corrections were made, were found to be as follows :—

	Annealed.	Hardened.
Medium steel, ...	2·366°	2·477°
Hard steel, ...	2·148°	2·309°

Showing that the hardened metal contains an excess of heat in comparison with the same metal when annealed.

(2) He also took heating curves of hardened steel, and found that the liberation of the latent heat of hardening is rendered evident by characteristic accelerations in the progress of the heating.

Thus, these facts clearly demonstrate that it is incorrect to say that the inversion is complete after rapid quenching and hardening, for they show that at least some of the inversion is suppressed. On the other hand, however, it must be admitted that there is no direct thermal evidence which definitely proves that the inversion is entirely suppressed when steels are rapidly quenched.

Since the conclusion which Grenet came to in regard to the hardness being due solely to the fineness of structure is, in the sense he referred to it, dependent upon the transformation having taken place, it does not appear to be correct (1st) because the transformation is certainly not complete, and (2nd) what evidence we possess on this aspect of the question strongly suggests, if it does not actually prove, that the suppression is complete.

The fineness of structure, as Grenet uses the term, does not refer to the molecular constitution, but to the crystalline dimensions of the decomposition products resulting from the inversion—*i.e.*, to the cementite and ferrite which he considers are formed under the conditions of cooling obtained on quenching.

This idea of the hardness being associated with fineness of structure, though from quite a different standpoint to that taken by Grenet, has been advocated in a good many instances by Beilby, notably in the passage already quoted in the chapter relating to Deformation and Strain-hardening.

According to this theory, hardening results from the formation at all the internal surfaces of slip or shear of mobile layers similar to those produced on the outer surface of polishing. These layers only retain their mobility for a very brief period, and then solidify in a vitreous, amorphous state, thus forming a cementing material at all surfaces of slip or shear throughout the mass. Beilby uses the terms amorphous and vitreous in the following sense:—Amorphous = non-crystalline, or the state in which the molecules are not marshalled in crystalline order and orientation. The addition of the term vitreous is intended to narrow the somewhat wide field covered by the term amorphous, as Beilby uses the combined terms " vitreous amorphous " for substances which in some degree resemble the glass-like form assumed by the silicates when they are solidified from the molten state. In recent years Beilby's work has attracted a great deal of attention from metallographists, and has been made use of to explain many phenomena of a widely different nature. Thus, Osmond says[1]:—" When two grains possessing different orientation touched one another, their respective reticular systems could not interlock, and there were strong reasons for the belief that there existed between the two grains a sort of amorphous envelope, the average thickness of which was of the same order of thickness as the crystalline molecule. If it was assumed, which it was admissible to do, that in the case of a hardened steel the average diameter of the actual grain —invisible under the microscope—was also of the same order of size, the idea might be entertained that in the hardened steel the iron might be amorphous. That would correspond to Beilby's 'Hard Iron.' "

Logically to apply Beilby's theory of hardening metals by cold working to the question of hardening metals by quenching from moderately high temperatures, it is, however, necessary to show that during the very short period of the quenching process the mass undergoes some internal movement on the surfaces of slip, or gliding planes. In the case of certain copper-aluminium alloys which possess almost the same physical characteristics as carbon steels, both as regards their constitution and the power of hardening by quenching, it was first shown by the author[2] that during quenching the crystals are subjected to internal slip on the cleavage planes, which produces prolific crystal twinning. This crystal twinning is not like the crystal twinning which is so often seen in annealed metallic specimens, where there are only one or two narrow strips or twins in each grain, for in quenching these alloys the number of twin formations are really too numerous to be counted (see photo-micrographs Nos. 67 and 68, which were taken from the same area after rotating the specimen through an angle of about 180°, with the use of oblique light). In a similar manner it has been shown by Carpenter and the author that exactly the same effect is produced during the quenching of carbon steels. The twinning effect produced in steels is illustrated in the photo-micrographs Nos. 72 to 74.

---

[1] Discussion on Grenet's paper.

[2] *Zeitschrift für Metallographie*, 1913.

Incidentally, it is worth noting that the microstructures of the copper-aluminium alloys mentioned above, and also of the carbon steels, indicate that when they are properly quenched from above the temperature at which the solid solutions break up into their constituents, they are constitutionally homogeneous. From this, along with the thermal evidence, it is quite reasonable to conclude that the inversion is entirely suppressed, and the solid solution which exists at high temperatures is preserved at the ordinary temperature by quenching. Hence the following account is the theory of hardening advanced by the author and jointly extended with Professor Carpenter.

The fact that twinning of the crystals is brought about by quenching these alloys conclusively proves that intercrystalline motion or slipping occurs. Since this has been established, it becomes possible to extend the theories that have been formulated by Dr. Beilby, and which are now generally accepted, for the hardening of metals by cold working to the hardening that is produced by quenching steels and certain other alloys. The only condition it is necessary to suppose, and there are indeed very good reasons for the supposition, is that the hard amorphous, vitreous layers that are formed on the cleavage planes during the internal slipping or twinning are retained by quick cooling. Dr. Beilby has shown that when metals containing these amorphous layers are heated, the latter return to the more stable crystalline form—that is, they recrystallise—and that the temperature at which this occurs varies with the particular metal or metallic alloy. Hence, if the rate of cooling is sufficiently quick, the temperature of the mass will be lowered below that at which recrystallisation takes place, the vitreous amorphous layers formed on the cleavage planes will be preserved and hardening will result; it would then follow that the final cause of the hardening which is produced by quenching is exactly the same as when metals are hardened by deformation by cold working. In the case of carbon steels and other alloys of a similar nature the actual strains that are set up in the mass, when they are quenched, and which give rise to twinning or slipping on the cleavage surfaces, are brought into action during the brief period the mass is cooling. Hence, whilst the metal is undergoing intercrystalline slip and the amorphous layers are being formed, the chances for these layers to recrystallise become less and less as the cooling proceeds, or it may be that a large proportion of the slipping which undoubtedly occurs, actually takes place at a moderately low temperature, and below that at which the amorphous layers are able to recrystallise. It is, however, necessary to consider if this idea is in keeping with known facts.

1st. The theory is applicable to all alloys, whether they contain iron or not, which can be hardened by quenching.

2nd. By making use of Dr. Beilby's excellent work and theories, the hardening which follows the cold working of metals, and that which is produced by quenching certain alloys, is due to the formation of amorphous layers on the cleavage planes. In both cases these layers are produced by intercrystalline movement or slip. The precise agencies, by means of which the intercrystalline slipping is brought about, are, however, somewhat different in the two cases.

3rd. It agreed with one of Osmond's latest statements on this question, viz. :—" If it were assumed, which it was admissible to do, that in the case of a hardened steel the average diameter of the actual grain—invisible under the microscope—was also of the same order of size (as the crystalline molecule), the idea might be entertained that in hardened steel the iron might be amorphous. That would correspond to Dr. Beilby's 'hard iron.' "

4th. In some respects it resembles Grenet's idea in regard to "fineness of structure," being the cause of hardening. The only difference being that in this case the fineness is regarded as a molecular fineness of one constituent only, whereas Grenet refeis to it as meaning a crystalline fineness of two or more constituents.

5th. Properly quenched carbon steels, when carefully examined under the microscope, show twinning of the crystals in a most pronounced degree, Since it has been definitely proved by Dr. Beilby that the hardening of metals which is produced by straining at moderately low temperatures is due to the formation of amorphous layers at the surfaces of slip, it follows that the twinning produced by quenching also gives rise to similar amorphous layers. The fact that crystal twinning is preserved at the ordinary temperature after quenching is a strong indication that these layers are also retained, and it is this cement which prevents the twin crystals re-uniting again.

6th. So far as can be judged from the present state of our knowledge, there is only one property of quenched steels which does not support this view—viz., all carbon steels are magnetic, no matter how energetically they are quenched from any high temperature. This is a very important fact, and should not be overlooked; nevertheless, there are now many metallurgists who are of the opinion that the magnetic properties are not definitely and entirely associated with α-iron. It is, for example, quite reasonable to suppose that the above-mentioned amorphous layers, which in quenched steel should be regarded as γ-iron, are magnetic; or that γ-iron when in the molecular condition is magnetic.

It should perhaps be pointed out at this stage that the degree of hardness is not considered to depend entirely upon the amount of crystal twinning, but more upon the nature of the amorphous layers that are produced thereby, as well as certain other factors, which will have to be considered later. As regards the effect of twinning *per se*, the fact that mild steels containing, say, 0·20 per cent. of carbon when effectively quenched from temperatures above 900° C. are seen to be a mass of twinned crystals, but are, nevertheless, very soft in comparison with quenched specimens containing 0·90 per cent. of carbon, seems to indicate that the degree of hardness is not governed entirely by the amount of twinning that is produced.

This is really not surprising when the experimental facts that have been established by Dr. Beilby are taken into account. He has shown that the amorphous layers which are produced by cold working possess different properties in different metals, and it is safe to say that the properties, such as hardness, etc., of the amorphous layers produced in metallic alloys will very largely depend upon the chemical composition of the alloys and molecular constitution of the layers.

Moreover, the internal molecular or osmotic pressure of carbon steels at temperatures below the solidus and within the γ range increases as the percentage of carbon is raised to 0·90, the temperature at which the γ solid solution can exist in a stable condition is thereby lowered, and the range of temperature through which the amorphous layers have to be cooled is, in consequence, considerably lowered and narrowed. It is, therefore, only natural to assume that the thickness of the amorphous layers will increase as the carbon is raised to 0·90 per cent., because the range of temperature through which they may be recrystallising is both lower and less. With higher percentages of carbon than 0·90 exactly the reverse phenomena set in—viz., the osmotic pressure decreases and the possibility of the amorphous layers recrystallising is greater.

In regard to the nature of the amorphous layers themselves, there are two points to be considered :—

First. Molecular packing, and second, the chemical composition of the amorphous layers.

It has already been mentioned that whatever theoretical explanation is given for the hardening of pure carbon steels by quenching, to be of any real value, it must also be consistent with the physical data and hardening properties of the so-called special steels. Hence, before making any definite conclusions from the knowledge we now have, and the opinions that have been expressed upon this subject, it is necessary and advantageous at this stage to draw attention to some of the more important characteristics of the special steels.

The term special steel is usually applied to those steels which contain, in addition to carbon, notable quantities of such elements as nickel, chromium, tungsten, manganese, molybdenum, etc. Broadly speaking, the effect of the presence of the elements just mentioned, upon the critical points as they appear in pure iron and iron-carbon steels, is to retard the tendency for the transformation, from the γ solid solution into α-iron and carbide, to take place. In certain cases the tendency in this direction, which may be conveniently regarded as a kind of automatic brake, is sufficient when the steels are even slowly cooled from moderately high temperatures to completely obstruct all the critical points or ranges. Thus, without giving a description in this chapter of the new carbides that are formed in these steels, it can be safely asserted that the combined action of chromium and tungsten of chromium and molybdenum along with carbon, and of nickel or of manganese along with carbon, is such that the operation of rapid cooling by quenching, which is necessary to suppress the critical points that occur when carbon steels are slowly cooled, can be dispensed with.

When the critical points have been suppressed by the addition of any of these metals, the steels are in what is known as the austenitic condition, and their microstructure partakes of polygonal crystals, as illustrated in fig. 168. There is, however, no doubt that the general properties of the different classes vary within very wide limits. For example, Sir R. Hadfield's manganese steel is practically non-magnetic at the ordinary temperature, and so extremely hard under the tool that it cannot be machined, but the hardness of the same material, according to the Brinell ball test, is only about 200 as compared with that of 700 to 850 for hardened carbon steel. Nickel steel containing about 25 per cent. of nickel is also non-magnetic, but is relatively soft by whatever method it is tested. In the case of the chromium-tungsten and chromium-molybdenum high-speed cutting steels, when cooled from very high temperatures, after which they are in the so-called austenitic condition, they are rather strongly magnetic and very hard. At this stage it should perhaps be mentioned that there are some misleading statements in the literature on high-speed steels, to the effect that at their hardest these steels are relatively soft. In certain cases, this may be the case; they are perhaps not quite so hard as the hardest quenched carbon steels, but the difference in this respect is very slight, and many of the brands upon the market are not inferior, in their degree of hardness, to carbon steels, at least when tested by Brinell's method. It is, however, quite well known that the relative hardnesses of different metals are not the same when tested by different methods, and some of the causes for these variations will be discussed.

For the time being it may be safely asserted that from the physico-chemical point of view the principal difference between the pure carbon steels and the so-called special steels which come under the class just now referred to, is that with the former the suppression of the carbide change, or separation, can only be brought about by external agencies, such as very rapid quenching from high temperatures, whilst in the latter steels the special elements present give rise to the formation of new carbides, which, no doubt, owing to their higher molecular volume, or molecular weight, exert a greater osmotic pressure when in the γ-iron solution, and lower the temperature at which the carbon—as carbide—separates from solution, and also decrease the velocity of the change. In other words, the action of these added elements is such that rapid quenching can be dispensed with, and the resulting steels are in the same physico-chemical state as rapidly quenched carbon steels, the only difference being that in the former the crystals are unstrained and not twinned, whilst in the latter pronounced twinning is produced by the quenching.

"In both cases the thermal or carbide change is inhibited by pressure, but when this is brought about by external means crystal twinning occurs, whereas when all the necessary pressure is already inherent in the mass no internal crystalline disturbance occurs, because the crystal and molecular units are not thereby interfered with. That is to say, when quenching is necessary intercrystalline movement takes place, and hardening is brought about in the same manner as the hardening by cold working. When the pressure already exists as osmotic pressure, all the internal molecular and crystal units are subjected to the same pressure at any given moment, and no internal dislocation occurs. Under these latter conditions the only hardening, if any, that is produced, is due to the larger quantity and nature of the added elements which are held in solution by the γ-iron, just in the same way that a steel containing, say, 0·9 per cent. of carbon is harder than one with 0·2 per cent. when both are at a temperature of 900° C."[1]

From the above it will be evident that the amount of twinning produced by the suppression of the inversion will, broadly speaking, be proportional to the amount of the inversion which has to be suppressed by the external quenching, or inversely proportional to the osmotic pressure of the special elements present. Hence twinning is entirely absent when the necessary pressure is supplied by sufficient nickel or manganese.

---

[1] Carpenter and Edwards, *loc. cit.*

As regards the statement that the amount of twinning will be proportional to the amount of the inversion which has to be suppressed by external means, such as quenching, or inversely proportional to the retarding influence of the special elements present, it should be noted that it is difficult to define exactly the term "quenching." For example, a given rate of quenching, which might be regarded as slow for carbon steel, might legitimately be regarded as rapid quenching for a special alloy steel. The following facts will, no doubt, make this point much more intelligible. If two samples of steel of about a cubic inch in volume, and having the following composition :—

Carbon Steel.	Carbon-chromium Steel.
0·9 per cent. carbon.	·63 per cent. of carbon. 6·00 ,, chromium—

are placed in a furnace at about 1,000° C., and then allowed to cool in the furnace over a period of, say, two hours, they will both be found to be quite soft. If, however, they are taken out of the furnace and allowed to cool in air, taking about half-an-hour to reach the ordinary temperature, the carbon steel will be very slightly harder than when cooled in the furnace, whereas the chromium steel will be very much harder. The actual figures for the chromium steel are :—

Cooled in furnace, ...	281	Brinell hardness.
,, air, ...	642	,,

Mr. J. C. W. Humfrey, who has carefully considered the question under discussion, also concludes that the hardening of steel, etc., by quenching is directly due to the formation of the amorphous phase.[1] The only difference between Humfrey's views and those advanced by Carpenter and the author relates to the manner in which the amorphous phase is brought into existence. Thus he says :—"An allotropic change must be considered as being essentially accompanied by a change in the internal structure of the molecules—*e.g.*, a re-organisation of the atoms composing them or a change in their number. Thus, we have the two gaseous allotropes of oxygen, the common gas in which each molecule contains two atoms, and ozone in which each molecule contains three atoms. When an allotropic change takes place in a crystalline body we must imagine a similar internal re-arrangement of the atoms in each molecule; and, if the new form which the molecules take involves a corresponding change in the external forces which they exert upon one another, then the previously existing space lattice may become unstable, and a fresh one may be formed characteristic of some other crystal form. But before the re-organisation can be completed there must, at least temporarily, be a state of disorder, and it is during this disorder that the author (Mr. Humfrey) considers that the structure must be considered as amorphous. The intermediate amorphous state may be realised as corresponding to the liquid which would be formed by the fusion of the solid phase stable at the lower temperatures if the conditions could be so adjusted that the subsequent recrystallisation were avoided." He considers that this condition is obtained when carbon steels are quenched, by lowering the temperature of the inversion below that at which the amorphous phase—formed as a first step in the change—can recrystallise into α-iron. In special steels the same effect is produced without rapid quenching by the added elements lowering the temperature of the change.

---

[1] *Proceedings of the Faraday Society*, 1914.

It will be noticed that there is exceedingly little difference between this theory and the one previously considered. In both cases the hardness is considered to be due to the amorphous phase, but in one this is supposed to be spontaneously formed, whilst in the other the internal straining as revealed by crystal twinning and caused by the quenching stresses are supposed to be the cause of the formation of the amorphous phase.

It should be noted that there is some difficulty in understanding how the amorphous phase which must be regarded as the same physico-chemical state as the liquid can possibly come into existence spontaneously at a temperature much below the liquefying point. It must be remembered that a change from the crystalline into the amorphous or liquid variety necessarily involves an absorption of energy, and it scarcely seems possible that an undisturbed mass which is cooling and, therefore, freely parting with energy, in the form of heat, can at the same time absorb from its surroundings the energy that is necessary to convert it into the amorphous state.

Another paper which should be carefully studied is that by Mr. Andrew M'Cance.[1] His chief conclusion is that:—" In a quenched and uniformly hardened steel the carbon is in the state of solution, and it retains a portion of the iron in the γ condition—the proportion increases very rapidly with the carbon content. The majority of the iron is, however, in the α condition, but, owing to the restricted mobility during the period of quenching, the crystalline units are not homogeneously oriented, and the hardness of quenched steels is due to this condition, which is similar to that of 'interstrain.' The hardness is interstrain hardness."

It is an exceedingly difficult matter to decide the exact difference between this view and those just considered. Perhaps the most important is that Mr. M'Cance considers that crystallised α-iron is the chief cause of hardness, whereas in the others the hardness is attributed to amorphous iron plus amorphous carbide. In all, it should be noted that the hardness is retained as a result of what Mr. M'Cance describes as a state of interstrain.

Mr. J. H. Andrew [2] has recently published a paper on this subject, and arrives at practically the same conclusion as M. Grenet.

---

[1] *Journ. Iron and Steel Inst.*, 1914, No. 1.
[2] *Zeitschrift für Metallographie*, 1914.

SPECIAL STEELS.

CHAPTER XVI.

INFLUENCE OF INITIAL TEMPERATURE AND RATE OF COOLING.

The so-called "special alloy steels" are those steels which contain notable quantities of one or more elements than iron and carbon. These elements are intentionally added to the steel in order to modify its physical, mechanical, or chemical properties, and thus render it more suitable for a specific purpose. It is true that even in what are generally regarded as ordinary carbon steels varying percentages of manganese are invariably used, but, broadly speaking, the object of using that element in such cases is more to reduce any oxide of iron which may be contained in the liquid steel, and to neutralise the effect of sulphur by forming manganese sulphide, than to impart any special property to the mass.

It is well known that the properties of carbon steels may be modified simply by varying the rate at which they are cooled from moderately high temperatures. Thus, a pure carbon steel may be made as hard as glass and exceedingly brittle by quenching in cold water from about 900° C., or quite malleable and ductile by allowing it to cool slowly from the same temperature. Almost any stage between these two extremes of brittleness and ductility can be obtained by controlling the rate of cooling, providing the mass be sufficiently small. This variation in the mechanical properties is due to differences in the internal structure of the material. An increased rate of cooling has the effect of lowering the temperature at which the carbide or Ar_1 change occurs, and by lowering the temperature of this inversion the carbide has less opportunity to develop or coalesce. Hence the properties of a carbon steel containing, say, 0·9 per cent. of carbon may be modified within wide limits as a result of the carbide possessing different degrees of fineness.

With carbon steels it is only possible to bring about the necessary variations in the rates of cooling when the mass of steel is small. In other words, these very remarkable differences in the properties are produced by comparatively slight differences in the cooling rates. For example, the steel is hard and brittle if the time taken in cooling from 900° C. be only a few seconds, but malleable if the time taken be, for example, ten minutes or even less. Hence, it is obviously impossible to bring about a marked change of hardness and tensile strength throughout the mass of a large carbon steel forging by hastening the cooling. This difficulty can be completely overcome by the addition of such elements as nickel and manganese, which may be regarded as producing an effect of the same order as quenching. They lower the temperature of the carbide change, and thus influence the physical and mechanical properties of alloy steels in a manner similar to that of quenching. By varying the percentage of nickel or manganese, the temperature of the carbide change can be lowered to any degree down to the ordinary temperature, and consequently steels with almost any desired properties can be readily obtained. There is one great advantage in the use of these special alloy steels—namely, that their properties are modified from within, and, therefore, practically the same quenching effects are obtained all through large masses of the materials.

Concerning carbon steels and the influence of initial temperature and varying rates of cooling, it must be admitted that the literature on this subject contains many unsatisfactory references to the time factor. Whilst, with regard to the rate of cooling, such statements as "slow," "hastened," and "quick" may be convenient, they have no real meaning, and are absolutely unsatisfactory from a scientific standpoint. The same lack of precision is manifest in the descriptions of the thermal magnitude of, say, the carbide critical points, for these are frequently stated to be "large," "medium," or "small," without any indication as to whether such differences are real or only apparent. During the early stages in the development of physical metallurgy it was not surprising that such general but scientifically inexact terms should be used, but there are very definite indications that this will not continue in the future, and that more exact researches on the quantitative influence of time, etc., will lead to the discovery of important facts.

The most important, and, indeed, almost the only published investigations dealing with the quantitative examination of the influence of initial temperature and varying rates of cooling of carbon steels are those by Benedicks [1] and Howe and Levy.[2]

Benedicks' work relates more particularly to the quenching velocities of varying quenching media, and the effect of different rates of cooling upon the critical points of steel.

Messrs. Howe and Levy have made an extensive series of observations on the effect of cooling a steel with 0·92 per cent. of carbon from 800° C. and 900° C., at varying determined rates, upon (*a*) the temperature of the Ar_1 transformation and its magnitude, (*b*) the microstructure, and (*c*) the tensile properties. The more important facts they observed are contained in Tables XXVI. and XXVII., and the graph in Fig. 147. The chief conclusions drawn from these data are briefly summarised as follows :—

(1) Hastening the cooling lowers the Ar_1 from its equilibrium position of about 725° C. at least to 625° C. if not to 530° C.

(2) Raising the maximum temperature from 800° to 900° C. lowers Ar_1 slightly, about 5° C.

(3) Hastening the cooling at first increases the degree of recalescence at Ar_1, but later lessens it.

(4) The rate of cooling from 650° C. down does not affect the microstructure or the tensile properties unless the cooling as far as 650° has been at least relatively rapid.

---

[1] *Journ. Iron and Steel Inst.*, 1908, ii., pp. 218 to 221.

[2] *Ibid.* 1916, vol ii., p. 210.

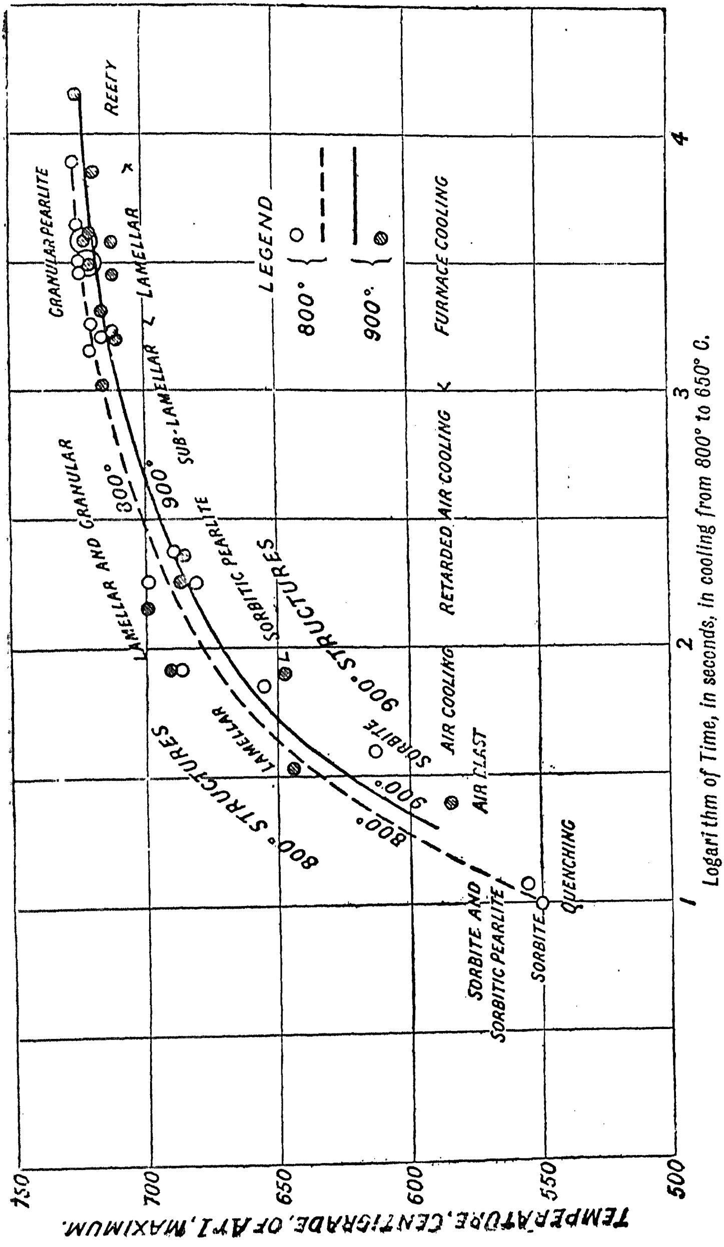


Fig. 147.—Descent of Ar_1 as the cooling accelerates and as the heating temperature T max. rises.

TABLE XXVI—COOLINGS FROM 800° C.

Treatment.				Results.							
Method of Cooling.		Time in Cooling.		Ar₁.			Tensile Properties.				Microstructures.
							Lbs. per sq in		Per cent.		
800 to 650.	From 650.	800 to 650		Temp	Length.		Tensile Strength.	Proportional Limit.	Elong. on 2″.	Reduction of Area.	
		min.	sec.		min.	sec.					
In furnace	In furnace	129	0	725-726	24	0	85,330	40,688	24	38·2	Granular pearlite with many fine points but clearly resolved, and many large islands.
,,	In air						87,380	40,688	24·5	40·7	
,,	In water						88,600	35,805	22·5	42·6	
,,	In furnace	64	0	722	14	0	95,780	40,688	15·5	29·0	
,,	In air	54	0	724	11	0	..	..	..	..	Granular pearlite.
,,	In furnace	48	0	725	11	0	92,930	45,774	23	46·7	Granular pearlite.
,,	In air						93,490	49,015	25·5	50·8	
,,	In water						91,200	40,688	22	45·5	
,,	In furnace	54	0	722	9	0	88,140	..	22	35·7	
	,,	27	0	718	6	0	92,070	48,085	24	42	Fine granular pearlite.
	,,	30	0	719	5	0	..	..	..	..	,, ,,
Retarded air	,,	..		..	..		102,402	52,429	18	40·5	Chiefly fine granular pearlite.
							104,400	51,150	18	29·5	,, ,, ,,
Retarded in air		4	0	689	1	20	104,750	53,850	17·5	41·3	,, ,, ,,
,, ,,		3	0	699	1	05	..	..	..	..	Very fine granular pearlite.
In air	In furnace	3	0	681	0	40	109,461	51,150	19	37·3	Fine lamellar and beaded pearlite.
,,	In air						114,167	60,720	17	34·5	
,,	,,	1	25	687	0	35	..	..	..	..	Very fine granular pearlite.
In air blast		1	10	655	0	25	..	..	..	..	Very fine lamellar pearlite.
,, ,,		0	40	616	0	25	117,450	58,390	15	30·2	Maximum lamellarity.
In lead		0	12	580	0	10	190,375	82,875	11	20·3	Sorbite with sorbitic pearlite.
In oil		0	10±	..	0	2 (?)	174,166	97,185	7·5	24·3	
In water		..		..	..		194,747	90,580	2·5	2·1	Martensite.

TABLE XXVII.—Coolings from 900° C.

Treatment.						Results.							
Method of Cooling.		Time in Cooling.			Ar$_1$.			Tensile Properties.					
								Lbs. per sq. in		Per cent.			
900 to 550.	From 650.	800 to 650.			Temp. °C.	Length.		Tensile Strength.	Proportional Limit.	Elong. on 2″.	Reduction of Area.	Microstructures.
		hrs.	min.	sec.		min.	sec.					
In furnace	In furnace	3	55	0	726	32	0	..	..	..	..	Lamellar to reefy pearlite.
,,	,,	2	0	0	721	18	0	107,100	43,485	5	6	Course lamellar pearlite, no divorce.
,,	In air	2	0	0	721			109,115	40,688	8·5	15	
,,	In water	2	0	0	721			110,740	25,575	5·0	7·5	
,,	In air	0	53	0	722	16	0	..	..	..	..	Course lamellar pearlite.
,,	In furnace	0	63	0	719	13	0	111,200	35,805	9·5	14·8	Lamellar pearlite.
,,	In air	0	34	0	716	11	0	..	..	..	..	,, ,,
Accelerated furnace		0	27	0	711	6	0	112,939	40,920	9·5	17·9	Sub-lamellar pearlite.
Retarded air	In furnace	..			685	1	20	134,525	46,035	10·5	14·3	,, ,,
In air	,,	0	0	80	647	0	45	142,450	61,380	8·5	13 9	Sorbitic pearlite.
In air blast		0	0	25	585	0	15	141,944	56,265	9·5	13·9	
In lead		..			..	..		200,560	91,580	4	4·2	Sorbite.
In oil		..			..	..		178,442	172,102(?)	7·5	15·3	
In water		..			..	..		204,223	146,528	2	7·9	Martensitic.

As indicating the remarkable ease with which the mechanical properties of carbon steel can be modified by carefully controlling the heating and cooling, it may be useful, briefly, to mention[1] the Sandberg Sorbitic Steel Co.'s method of treating tramway rails, *in situ*. The process consists in causing a flame to travel slowly along the surface of the rail under treatment. The speed at which the flame passes over the surface is so regulated as to cause the steel to be heated above the highest thermal change to the required depth. This heating is followed by the application of a stream of water to the heated surface. The operation is continuous, and the whole equipment is carried on a truck which runs on the tram track. The microstructures corresponding with the three positions A, B, and C, Fig. 148, are shown in Figs. 149, 150, 151, and 152.

With regard to the thermal magnitude of the carbide change as seen in an inverse rate curve, it is well known that the apparent size or intensity of this transformation is governed to a considerable extent by the rate of cooling. The effect is such as to give a smaller peak on the curve as the rate of cooling is increased. It is, however, very important to note that in most instances this apparent change in the arrest at the critical point does not necessarily correspond with any alteration in the total quantity of heat that is evolved during the transformation. Other things being equal, the duration of an arrest, or the size of a critical point on a cooling curve is inversely proportional to the rate of cooling. From this it follows that whilst the critical point appears to progressively decrease in magnitude as the rate of cooling is accelerated, the ratio $\frac{\text{duration of arrest}}{\text{rate}} = \text{constant}$, so long as the transformation is the same and it takes place completely at approximately the same temperature. It may, therefore, prove quite misleading to describe a critical point as small on the one hand, or large on the other, unless the rate of cooling is duly taken into account.

Brinell Hardness—

A 600.
B from 600 to 240.
C 240.

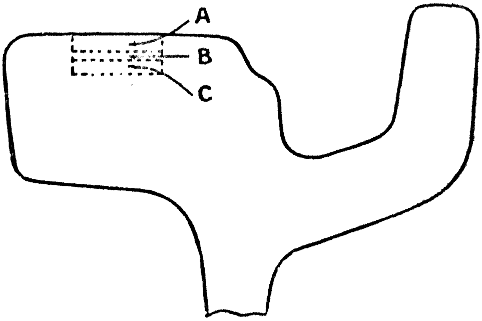


Fig. 148.—Diagram of worn rail, showing position from which micrographs were taken.

The study of the thermal magnitude of the carbide change with adequate reference to the rates of cooling might prove exceedingly interesting, more especially from the point of view of the constitution of special alloy steels.

---

[1] *Engineering*, April 5, 1918.

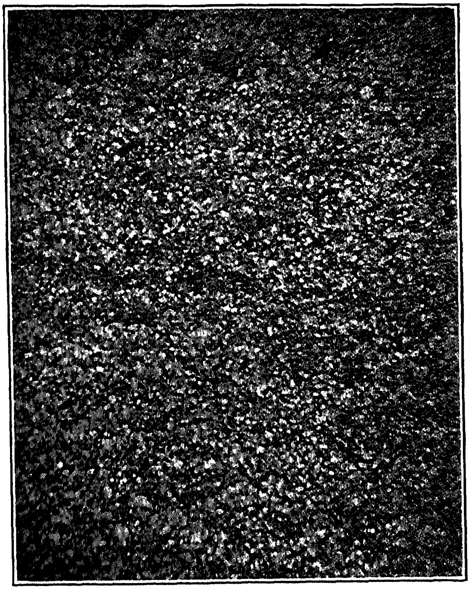


Fig. 149.—Micrograph × 100 diameters showing sorbitic structures $\frac{1}{8}''$ from surface of rail, corresponding to "A" in fig. 148.

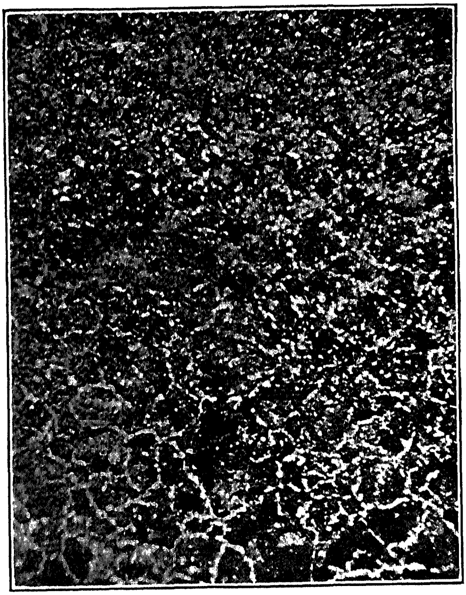


Fig. 150.—Micrograph × 100 diameters showing gradual change from sorbitic to pearlitic structure $\frac{3}{16}''$ from surface of rail, corresponding to "B" in fig. 148.

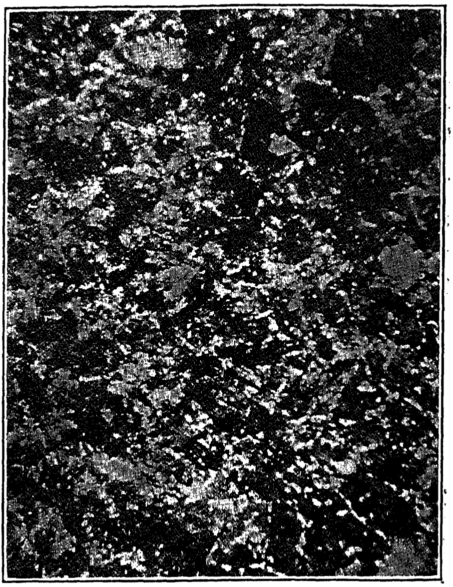


Fig. 151.—Micrograph × 100 diameters showing normal pearlitic structure $\frac{5}{16}''$ from surface of rail, corresponding to "C" in fig. 148.

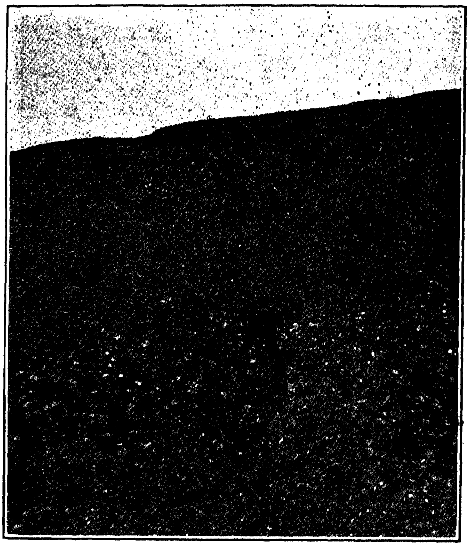
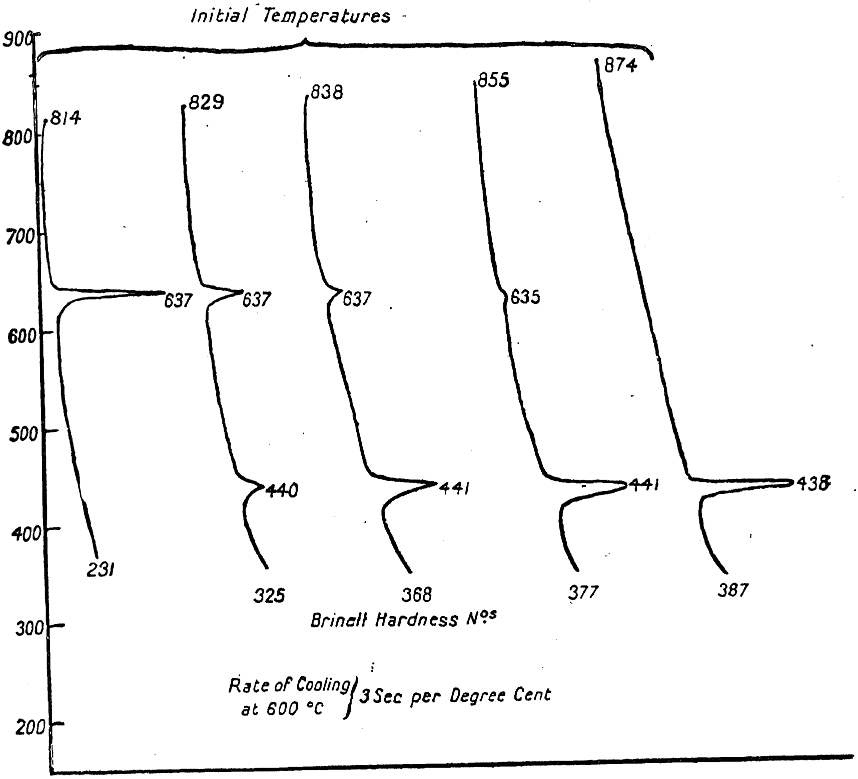


Fig. 152.—Fractured rail, enlarged five times, showing hardened portion of rail head.

In some of these steels it is quite possible that the thermal effect usually observed in taking cooling curves is merely the net result of two entirely different reactions. For example, the carbide which first comes out of solid solution and gives rise to an evolution of heat, may be an unstable compound, and the first stage in the reaction be immediately followed by the formation of a more stable carbide which absorbs heat during its formation. By making very careful determinations of the arrest periods obtained with known increasing rates of cooling and comparing the data



Carbon, ·33. Nickel, 3·14. Chromium, 1·61.

Fig. 153.

thus found as $\frac{\text{duration of arrest}}{\text{rate}}$, it should be possible to detect the presence of any such complication in the nature of the carbide change as is indicated above. Although the evidence is as yet incomplete the author believes that this kind of double transformation does occur in certain tungsten chromium steels. For, over one quite wide range of cooling rates the above-mentioned ratio is quite constant, but after a certain rate of cooling is passed this ratio suddenly increases, then remains nearly constant at this higher value before it decreases and is ultimately suppressed. If the data so far obtained can be supported by more carefully conducted experiments, it would mean that the net carbide change with slow cooling consists of two reactions, one of which is exothermic, and the other endothermic, and that the latter can be partly, if not completely, prevented with certain definite rates of cooling.

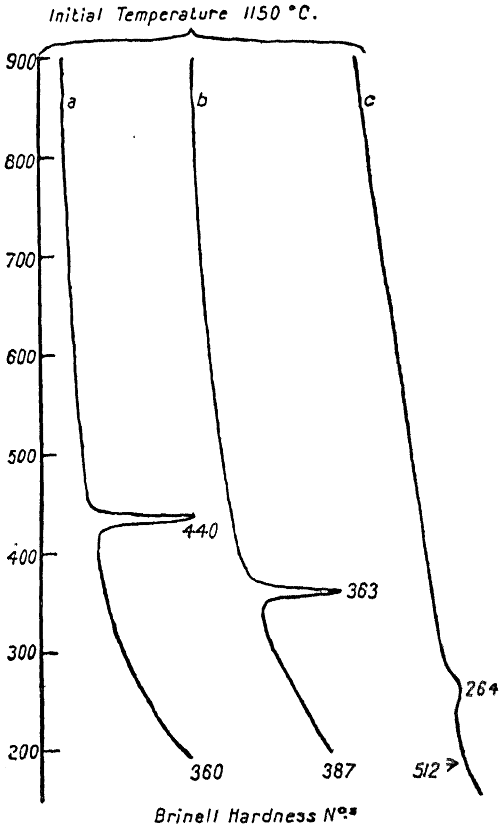
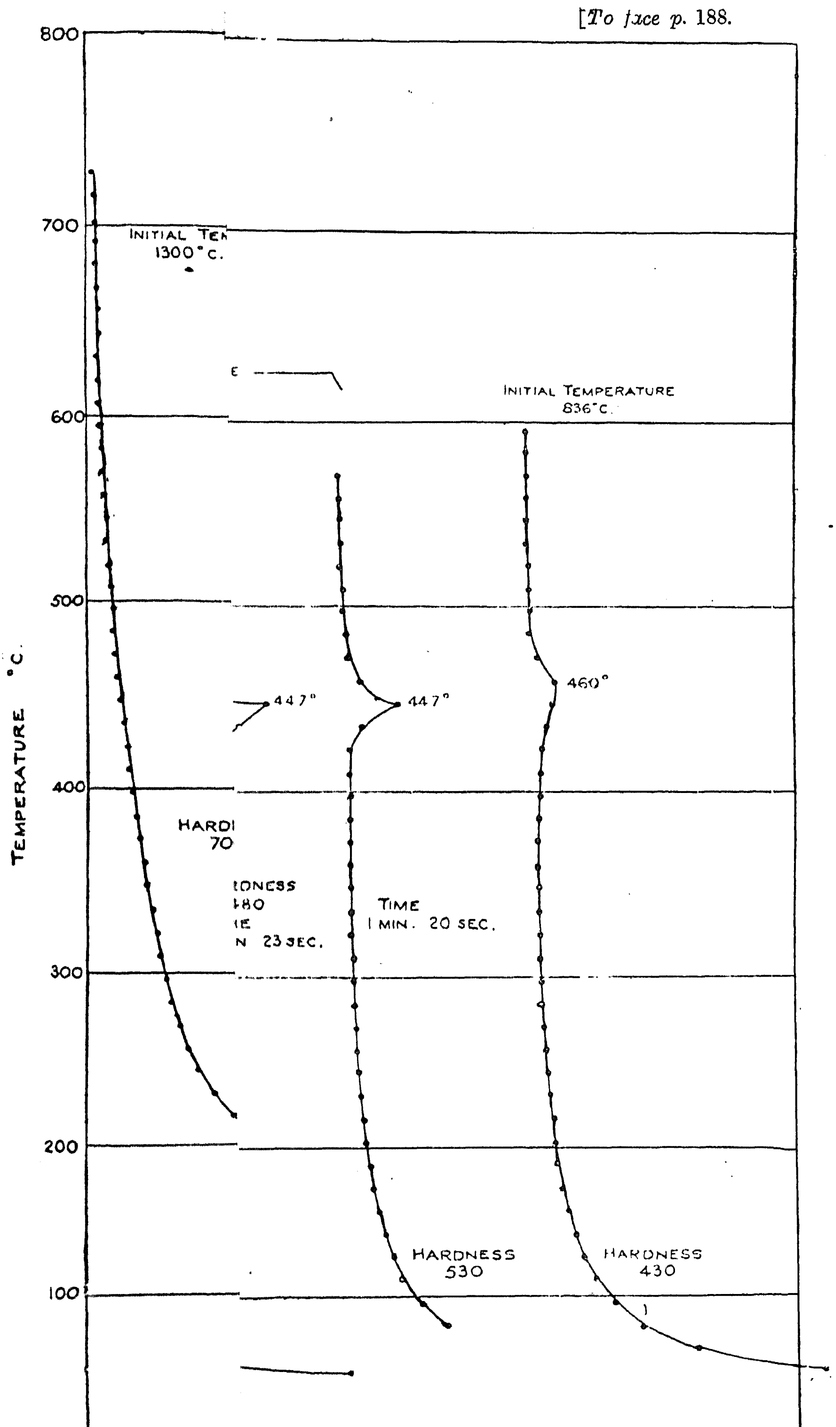


Fig. 154—Rate of cooling at 600° C. b = 0·5 sec. per degree C.
a = 3 sec. per degree C. c = 0·2 ,, ,, ,,

Many of the special alloy steels are far more sensitive to comparatively small variations in heat-treatment than carbon steels. Thus, the widely used nickel chromium steel containing approximately 3·0 per cent. of nickel, 1·5 per cent. of chromium, and ·35 per cent. of carbon is extremely sensitive to small changes of temperature over a certain limited range. Cooling curves of a steel of this kind are shown in Figs. 153 and 154. With the lowest recorded initial temperature, 814° C., it will be seen that there is only one heat change on cooling at 637° C., if, however, the initial


800
700
600
500
400
300
200
100
TEMPERATURE °C.
INITIAL TEr
1300°C.
E
INITIAL TEMPERATURE
836°C.
447°
447°
460°
HARDI
70
tONESS
+80
tE
N 23 SEC.
TIME
1 MIN. 20 SEC.
HARDNESS
530
HARDNESS
430

temperature is raised 15° C.—*i.e.*, to 829° C.—the evolution of heat at 637° C. is considerably smaller and a second one at 440° C. appears. As the initial temperature is further raised the magnitude of the upper change decreases, whilst that of the lower one increases, until, when cooled from about 874° C. or above, no evolution of heat occurs at the higher temperature. It will also be observed that with comparatively slow rates of cooling—3 sec. per degree—the initial temperature is practically without influence upon the temperature at which the low change takes place. It is only with the quickest rates of cooling that the temperature of the low change point is depressed. The Brinell hardness numbers of this steel, after each cooling, are given under the respective cooling curves. The fact that very high initial temperatures—above 874° C.—have no effect upon the thermal characteristics of the steel must not be regarded as indicating they are without action on the mechanical properties, for such is not the case.

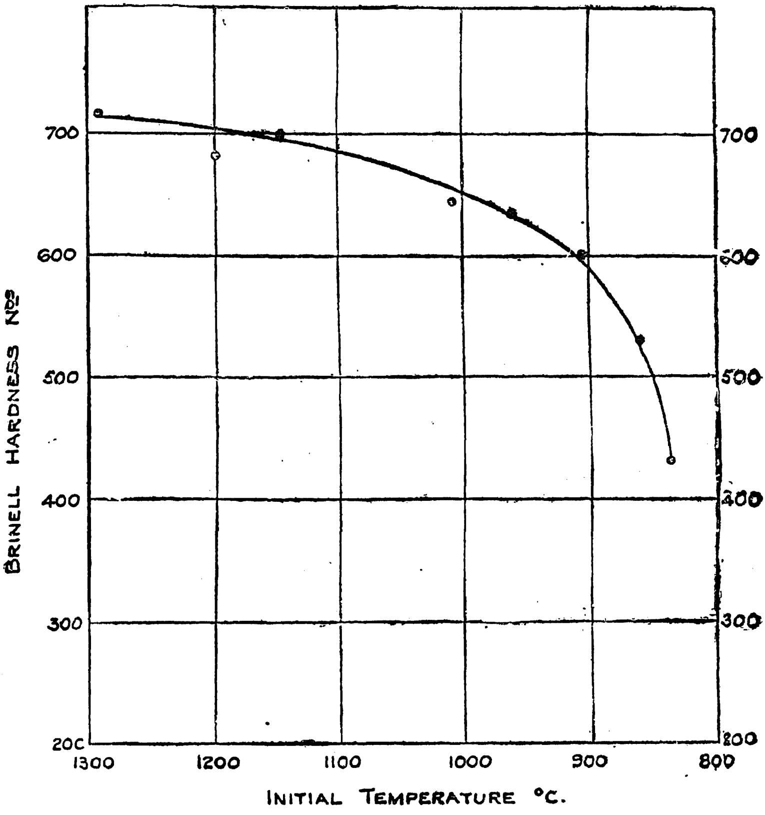


Fig. 156—Effect of initial temperature on hardness with air cooling.

The behaviour of other steels in respect to initial temperature and rate of cooling may be very different from that just considered, and although the amount of quantitative data is at present somewhat meagre, the case of chromium steels may be mentioned as showing quite different characteristics from the above. A set of cooling curves for a steel containing about 6·0 per cent. chromium and ·60 per cent. of carbon, as shown in Fig. 155. As will be seen many of these curves were taken at practically the same cooling rate from different initial temperatures. With this steel the nature of the carbide critical point, and the temperature at which it takes place, can be entirely modified, both by varying the rate of cooling and the temperature to which it is heated. The effect upon the Brinell hardnesses of heating this chromium steel to various temperatures followed by rapid air cooling is shown in Fig. 156.

From what has been said above it is scarcely necessary to state that the time factor, or rate of cooling, and the initial temperature should receive very careful attention in the study of all steels, and especially in the case of alloy steels. This should not be confined to a qualitative examination of these variables, but should be extended in such a way as to make it possible to construct constitutional diagrams in which they are both adequately represented. This could be done quite satisfactorily by taking the critical cooling rate as the rate at which the normal carbide change just begins to be depressed, and plotting these as verticals upon a triangular base—for ternary systems—in the same manner as is now done for temperature, see Chapter I.

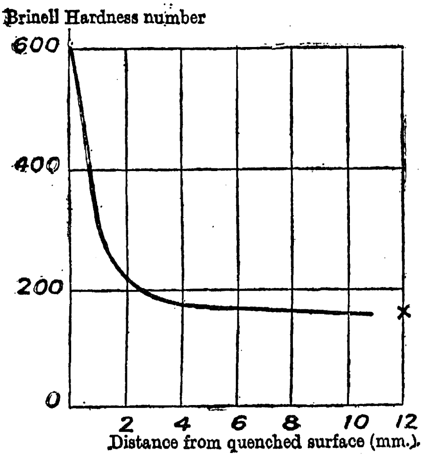


Fig. 157.—Depth of penetration of quenching influence in a Carbon steel.

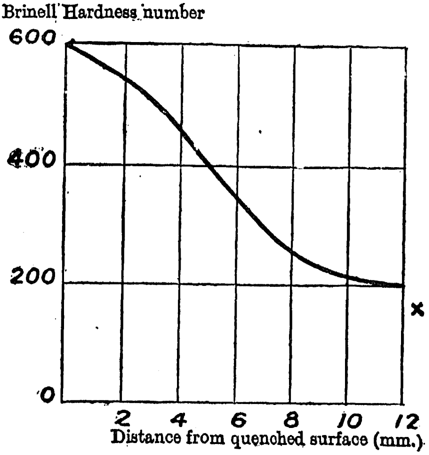


Fig. 158.—Depth of penetration of quenching influence in steel containing 6 per cent Nickel.

In a most interesting contribution to the discussion on a paper by Stead,[1] L. Grenet gave a series of diagrams which clearly illustrate the influence of various elements upon the hardening properties of steel. These diagrams, which are reproduced in Figs. 157 to 163, are not intended to represent

---

[1] *Journ. Iron and Steel Inst.*, 1916, No. 2, p. 117.

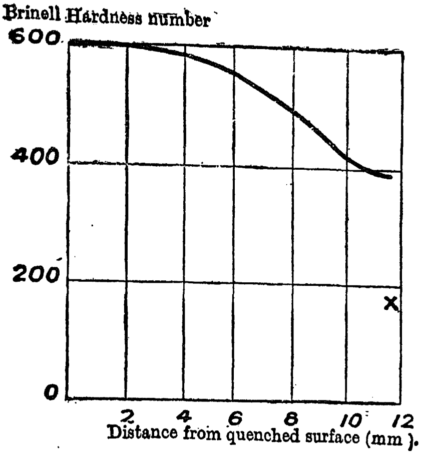


Fig. 159.—Depth of penetration of quenching influence in steel containing 10 per cent. Nickel.

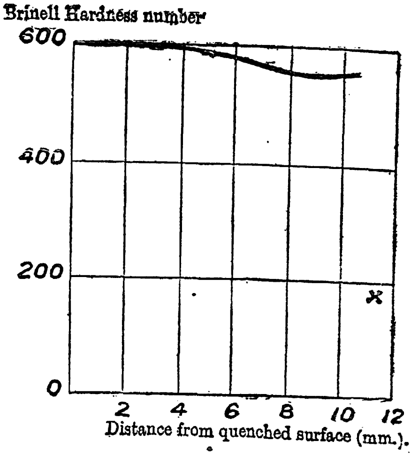


Fig. 160.—Depth of penetration of quenching influence in steel containing 14 per cent. Nickel.

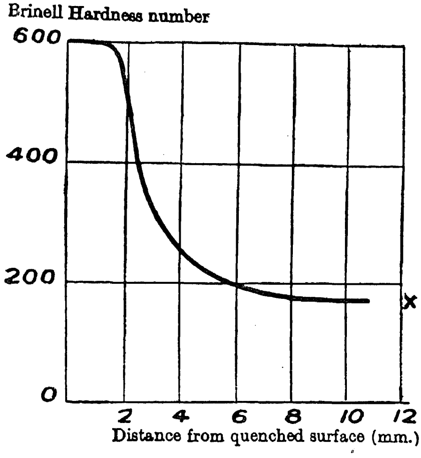


Fig. 161.—Depth of penetration of quenching influence in steel containing 1 per cent. Chromium.

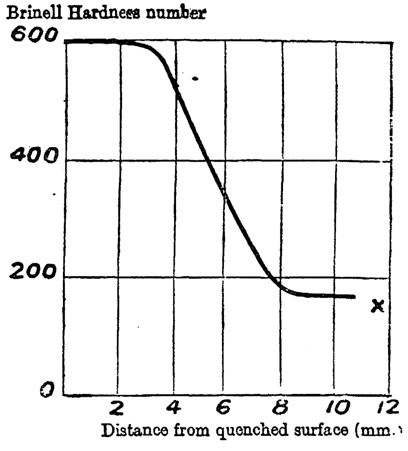


Fig. 162.—Depth of penetration of quenching influence in steel containing 5 per cent. Chromium.

the exact depth of penetration of the quenching effect, but they are comparable with one another. Concerning these figures Grenet says :—" As we are only concerned with an approximate representation, the unit selected is of no importance. Let it be considered as of the order of size of a centimetre. In all the curves X indicates the hardness of the steel at maximum softness.

" In a carbon steel the hardness, which is at its maximum in the neighbourhood of the quenched surface, decreases rapidly until it reaches a degree which remains practically constant, and corresponds with that of the steel as annealed at 850°, and softened to its maximum.

"In a nickel steel the hardness, which is at its maximum in the neighbourhood of the quenched surface, decreases fairly regularly until it reaches a degree which remains practically constant, and corresponds with that of the steel as annealed at 850°. The hardness of this steel, annealed at 850° C., approaches more closely, however, to the maximum hardness of the quenched steel the higher the percentage of nickel present, and diverges more greatly from the hardness of the steel at its maximum softness (annealed at a little below the temperature of the heating transformation) the higher the percentage of nickel (see Figs. 158, 159, and 160). For a chromium steel the hardness decreases more and more slowly in proportion as the percentage of chromium increases, reaching ultimately the hardness of the annealed metal, which is that of the steel at its maximum softness (see Figs. 161 and 162).

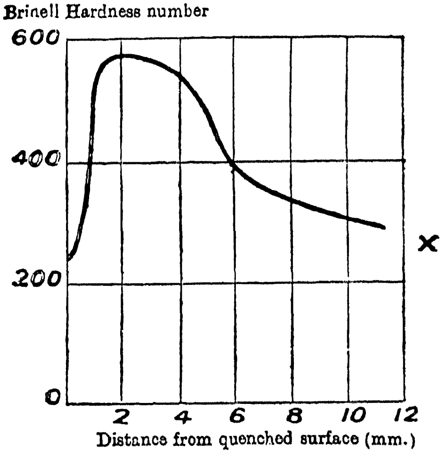


Fig. 163.—Depth of quenching in a manganese steel containing 1·20 per cent. of Carbon. As explained, and in order to form a concrete example, the units plotted as abscissæ represent 1 centimetre when the manganese percentage is 1·50 per cent. and 10 centimetres when this percentage reaches 12 per cent.

"The higher the percentage of chromium is raised the more important becomes the range within which the hardness is in the neighbourhood of its maximum. The fall in the hardness takes place ultimately fairly rapidly.

"The action of manganese is analogous to that of chromium, the transition from the range of softness to the range of hardness being more continuous. When the percentage of manganese is high enough, the areas near the quenched surface may become soft if the quenching suppresses the cooling transformation, and leaves the metal in the 'stable condition on heating.' No experiments have been made on the penetration of the quenching effect on manganese steels, and the curve shown in Fig. 163 is given only to serve for placing on record the train of thought based on the facts known.

"The proportion of any given element is increased to the degree to which it is desired to increase the penetrative action of quenching. Thus, to increase the action of quenching to greater depths nickel would be increased; to diminish the effect and confine it superficially the chromium would be raised, while, to render it more continuous in its effect, the manganese would be raised, or, better still, chromium-nickel steel would be employed."

In regard to the exact physico-chemical action of the alloy elements used in special steels, up to the present no really satisfactory theory has been put forward. This is not very surprising, in spite of the large amount of research work that has been published, when it is remembered that we do not know all the changes, and their theoretical explanations, which occur in the pure iron-carbon alloys. Attempts have been made to show the relation between the position of the elements in Newlands and Mendeléeff's "periodic tables," and their effects upon the properties of iron and steel, but they have so far met with little or no real success. Osmond [1] arranged a number of the elements in the order of their atomic volumes, found by dividing their atomic weight by their specific gravity :—

I.		II.	
Carbon,	3·6	Chromium,	7·7
Boron,	4·1	Tungsten,	9·6
Nickel,	6·7	Silicon,	11·2
Manganese,	6·9	Arsenic,	13·2
Copper,	7·1	Phosphorus,	13·5
		Sulphur,	13·7

He considered that the elements in column I., whose atomic volumes are smaller than that of iron (7·2), delay the Ar_3, Ar_2, and Ar_1 transformations, whilst elements whose atomic volumes are greater than that of iron (column II.) tend to raise the temperature at which those changes occur. There can be no doubt that this arrangement is quite inadequate, because the action of the above elements cannot be arranged in two simple columns, and also because it does not take into account the fact that they may form new compounds with the carbon and the iron. Nevertheless, it is more than probable that the chemical and physical action of the various elements upon iron and steel is in some way governed by their atomic or molecular constitution, and, if this be so, we may reasonably hope that some useful theory or law similar to the periodic classification of the elements will ultimately be discovered. Before this can be satisfactorily accomplished, however, the various chemical compounds which the elements are capable of forming, both with the iron and carbon, must be carefully isolated. In this connection the very careful work of Professors Arnold and Read on the determinations of the carbides which exist in annealed special steels cannot be too highly appreciated.

When we come to study a series of alloys containing more than two elements, the number of mixtures and experiments that are really required in order to obtain anything like a reliable idea of their properties are exceedingly numerous. In the case of steels, this fact is in many ways even more evident than in the majority of other alloys, because steel is so remarkably sensitive to comparatively slight variations or irregularities in its mechanical or heat treatment as well as in its composition. It is no doubt largely on nt of these difficulties that so far no single publication dealing with ːy steels can be legitimately regarded as embracing a complete list physical and mechanical properties of the particular series with which ıls. Further, as much less work has been done relating to the true co-chemical constitution of such steels, any attempt to formulate etical explanations of their peculiar and particular properties must sarily be of a tentative nature. Hence, in reviewing the large number perimental facts contained in the various scientific journals, it is an nely difficult task to decide what should and what should not be led in a book of this kind. This obvious difficulty is still further ısed because the investigators have frequently had widely different ses in view, and have, therefore, conducted their researches along ent lines.

---

[1] *Journ. Iron and Steel Inst.*, 1890, part 1, p. 38.

Nickel-Iron Alloys and Nickel-Iron-Carbon Steels.

1862 Sir Henry Bessemer[1] made some nickel steel ingots by melting lic nickel with wrought iron, but, owing to the presence of high sulphur phosphorus contents, the results he obtained were unsatisfactory. In

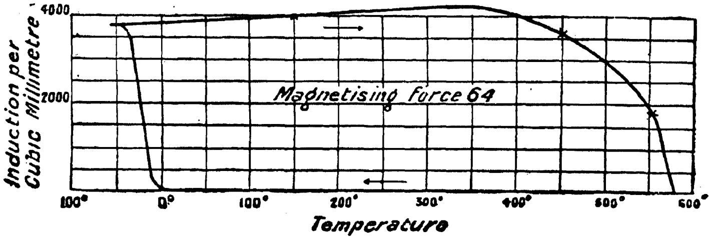


Fig. 164.

Mr. James Riley[2] published some valuable data relating to the anical properties of nickel steel. There seems to be no doubt that the mportant application of nickel steel on a large scale was in the case of ır plates made by Messrs. Schneider & Co., Le Creusot, France. The d States Navy subsequently used this kind of steel for the same pur- It was found that nickel steel armour plates were much superior ordinary Harveyised steel plates containing no nickel, even when the f the former had not been subjected to the Harvey treatment.

ofessor John Hopkinson, in 1889,[3] published the very interesting hat a sample of steel containing 25 per cent. of nickel was non-magnetic linary temperatures, but became magnetic on being cooled to slightly 0° C., and highly magnetic at a temperature of – 51° C. On returning ordinary temperature it remained magnetic, and only lost this property heated to 580° C. Hence this steel was capable of existing in two cal conditions in one range of temperature. The mechanical properties also found to be different, the magnetic sample possessing a higher tensile strength and a lower elongation. This was the first account of the irreversible transformation of nickel steel. These magnetic differences are clearly illustrated in fig. 164.

---

[1] *Iron and Steel Inst.*, 1895, No. 2.

[2] *Journ. Iron and Steel Inst.*, 1889, No. 1, p. 45.

[3] *Proc. Roy. Soc.*, Dec. 2, 1889, and Jan. 16, 1890.

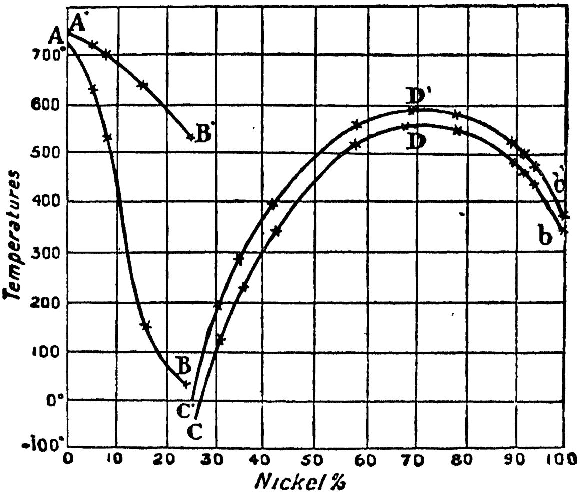


Fig. 165.

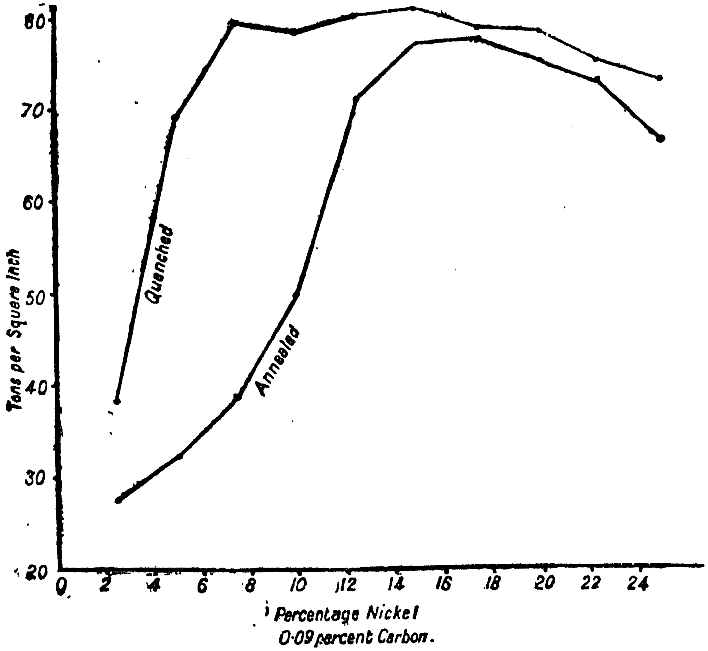


Fig. 166.

C. E. Guillaume [1] conducted an important investigation with a serie of steels containing from 12 to 45 per cent. of nickel, and definitely establishe the fact that the temperatures of the transformation points are progressivel lowered as the nickel is increased to about 25 per cent. With higher percentages they are raised and the nature of the transformation is changed The transformations in steels containing less than 25 per cent. are irreversible but reversible when the nickel content is above 25 per cent. Osmond examined a complete series of practically pure iron-nickel alloys, and determined the temperatures at which the magnetic changes occur both on heatin and on cooling. He embodied his results in the diagram (fig. 165). It i obvious from this diagram that as the nickel is raised from 0 to 25 per cent the transformation points are lowered and the irreversible range of temperature is materially widened.

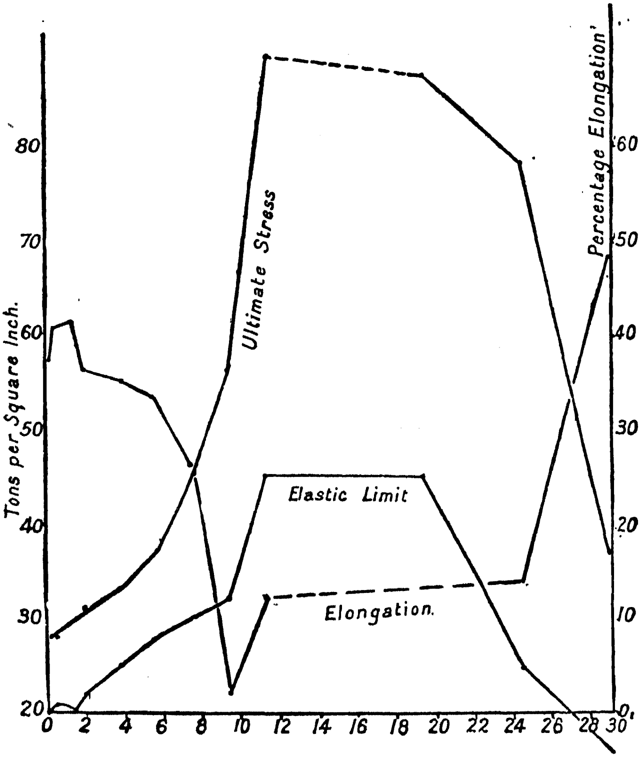
TABLE XXVIII.

Chemical Composition.			Breaking Load.		Increase of Breaking Load due to Hardening.
Carbon.	Manganese.	Nickel.	Reheated to Dull Cherry-red and Cooled in Sand.	Hardened in Water at Dull Cherry-red Heat.	
Per cent.	Per cent.	Per cent.	Tons per sq. in.	Tons per sq. in.	Per cent.
0·09	0·04	2·48	27·3	37·9	38·8
0·09	0·04	5·03	32·1	67·5	110·5
0·09	0·04	7·54	38·1	77·5	103·3
0·08	0·04	10·06	48·9	76·5	56·5
0·09	0·04	12·42	69·7	79·1	13·5
0·08	0·04	15·09	75·3	80·0	6·2
0·08	0·04	17·60	75·6	78·0	3·1
0·09	0·04	19·96	73·3	76·6	4·5
0·09	0·04	22·63	71·3	73·5	3·0
0·10	0·04	25·15	65·0	71·5	10·0

The tensile strength of what may be regarded as pure iron-nickel allo which are given in Table XXVIII., and plotted in fig. 166, were published the "Fonderies, Forges et Acieries de St. Etienne.[3] One of the most interesting features about these figures is that they show that, even with ve pure iron-nickel alloys which contain practically no carbon, their hardne can be substantially raised by quenching in water. They also show th the tensile strength of the annealed specimens is increased as the nick is raised up to about 17·6 per cent., after which there is a fall in that proper with additional nickel content. Professor Arnold [4] has also determined t mechanical properties of a remarkably pure series of nickel-iron alloys whi are in substantial agreement with the above. Sir Robert Hadfield's classic work [1] is probably the most complete published investigation of the gener properties of nickel-iron alloys, and should be carefully studied by tho interested in the subject. Some of these results are reproduced in Tab XXIX. and plotted in fig. 167. It will be observed that whilst Hadfielc

---

[1] *Comptes Rendus*, Jan. 25, April 5, June 18, July 26, 1897.
[2] *Ibid.*, vol. cxxviii., p. 306.
[3] Pamphlet published by S. Kirsch, 6 rue de la Bourse, Saint Etienne, 1894.
[4] *Inst. of Mech. Engs.*, 1914.



Percentage Nickel.
Fig. 167.

steels contained about 0·18 per cent. of carbon, and about 0·8 per cer of manganese, the results he obtained are in such close agreement wi those in Table XXVIII. that for all practical purposes the very complete da which he has published may be accepted as representing the properties the pure binary series.

Professors Arnold and Read [2] express the opinion that there is a defin alloy of iron and nickel corresponding to the formula $NiFe_7$. There is definite chemical evidence which supports this view, the chief evidence bei that there is a marked discontinuity in the mechanical properties of t alloys at or about 13 per cent. of nickel. This remarkable break is, howev readily accounted for by the effect of the nickel upon the temperature of t

[1] *Inst. of Civil Engs., Proc.*, vol. cxxxviii., pp. 1-125.
[2] *Inst. of Mech. Engs.*, 1914.

TABLE XXIX.

Analysis.			Unannealed Test Bars. Load in Tons per Square Inch.				Annealed Test Bars. Load in Tons per Square Inch.			
Carbon.	Manganese.	Nickel.	Elastic Limit.	Breaking Load.	Elongation.	Reduction of Area.	Elastic Limit.	Breaking Load.	Elongation.	Reduction of Area.
					Per cent.	Per cent.			Per cent.	Per cent.
0·19	0·79	0·27	19	31	35	56	20	28	37	52
0·14	0·75	0·51	20	30	36	62	21	27	41	63
0·13	0·72	0·95	25	33	31	53	20	27	41	63
0·14	0·72	1·95	26	34	33	55	22	31	36	53
0·19	0·65	3·82	28	37	30	54	25	33	35	55
0·18	0·65	5·81	28	41	27	40	28	37	33	51
0·17	0·68	7·65	31	49	26	42	30	45	26	41
0·16	0·86	9·51	42	85	9	18	32	56	2	2
0·18	0·93	11·39	65	94	12	24	45	89	12	26
0·23	0·93	15·48	55	94	3	2	..	68	1	1
0·19	0·93	19·64	47	91	7	6	45	87	5	4
0·16	1·00	24·51	32	77	13	14	25	78	14	8
0·14	0·86	29·07	25	38	33	44	16	37	48	51
0·16	1·08	49·65		not	tested		15	36	49	53

thermal critical points, in exactly the same way as the same effect is brough about in other alloy steels.

Nickel-Iron-Carbon Steels.

Although no reliable data seems to have been published relating to th relative segregation of nickel-carbon steels and ordinary carbon steels, i appears to be generally admitted that the presence of nickel tends to neutralis this evil. If this is indeed a fact, it is probably due to the nickel decreasin the solidification range of temperature by the formation of new carbides It has been shown by Arnold,[1] and also by G. B. Waterhouse,[2] that th presence of nickel in steel facilitates the conversion of the carbon from th combined into the graphitic state. Professors Arnold and Read[3] say:— "That as a 'black-steel forming' element nickel is, of all metals so fa investigated, the greatest graphite precipitater." It is probably owing t this action that pure nickel-carbon steels are seldom used, especially if hig nickel or carbon percentages are required. Under these conditions th presence of chromium or manganese is necessary to maintain the carbo in the combined state. The precipitation of graphitic carbon is apparentl due to the decomposition of nickel carbide, Ni_3C, which seems to be muc less stable, at a forging heat, than any other metallic carbide present i special alloy steels.

G. B. Waterhouse[4] has published an account of the mechanical propertie of a series of steels in which the nickel remained practically constant a 3·75 per cent., with the carbon varying from 0·4 to 1·83.

The chemical analyses of these steels are given in Table XXX., and th mechanical properties in Table XXXI. These results are particularly useful because the percentages of nickel closely correspond to what is generall aimed at in most nickel steel forgings, etc. The chief difference lies in th fact that the commercial steels invariably contain from 0·4 to 0·8 per cent of manganese, and sometimes from 0·5 to 1·5 per cent. of chromium. Th effect of nickel is clearly illustrated in Table XXXII., where a compariso is made between two of the nickel steels and two carbon steels containin about the same amount of carbon.

TABLE XXX.

Mark of Steel.	K	L	M	N	P	O	Q	R	S	T
Total carbon,	0·41	0·51	0·63	0·79	0·92	0·97	1·24	1·54	1·64	1·82
Nickel, .	3·79	3·79	3·76	3·81	3·79	3·75	3·81	3·82	3·82	3·79
Silicon, .	0·102	0·103	0·133	0·129	0·126	0·095	0·117	0·144	0·151	0·133
Manganese, .	0·086	0·054	0·050	0·051	0·047	0·058	0·057	0·054	0·047	0·051
Sulphur, .	0·013	0·014	0·014	0·014	0·014	0·014	0·015	0·014	0·015	0·016
Phosphorus,	0·007	0·008	0·008	0·008	0·008	0·008	0·008	0·007	0·009	0·009
Aluminium, .	0·01	0·01	0·009	0·01	0·009	0·011	0·009	0·01	0·01	0·01

---

[1] Discussion on Hadfield's paper, p. 131.

[2] *Iron and Steel Inst.*, 1905, No. 2.

[3] *Inst. of Mech. Engs.*, 1914.

[4] *Iron and Steel Inst.*

TABLE XXXI.—MECHANICAL PROPERTIES OF BARS HEATED AT 1,000° C. FOR 25 MINUTES AND COOLED IN AIR.

No.	Ni.	C.C.	G.C.	Elastic Limit.	Ultimate Stress.	Elongation on 2 inches.	Contraction of Area.
				Tons per sq. inch.	Tons per sq. inch.	Per cent.	Per cent.
K	3·79	0·41	..	21·67	40·28	26·0	44·75
L	3·79	0·51	..	22·52	44·24	21·0	39·05
M	3·76	0·63	..	25·01	51·52	16·5	26·27
N	3·81	0·79	..	29·84	60·55	14·0	21·27
P	3·79	0·92	..	35·04	69·42	8·0	14·08
O	3·75	0·97	..	35·76	70·01	7·5	8·39
Q	3·81	1·24	..	45·44	75·31	3·5	3·20
R	3·82	1·21	0·31	29·25	65·01	10·5	13·9
S	3·82	0·93	0·71	30·18	46·84	14·5	20·96
T	3·79	0·91	0·91	29·66	58·76	12·0	13·92

TABLE XXXII.—COMPARISON WITH CARBON STEELS.

Carbon.	Nickel.	Elastic Limit.	Ultimate Stress.	Elastic Ratio.	Elongation on 2 inches.	Contraction of Area.
		Tons per square inch.	Tons.		Per cent.	Per cent.
0·38	..	17·95	29·94	60·2	34·5	56·3
0·41	3·79	21·69	40·28	53·7	26·0	44·7
1·20	..	35·72	61·65	57·8	8·0	7·8
1·24	3·81	45·44	75·31	60·3	3·5	3·5

From his pyrometric investigations Waterhouse concludes that 3·75 per cent. of nickel lowers the temperature of the carbide change to 610° C., and that this change is practically unaffected by the carbon content.

In the pamphlet published by the "Fonderies, Forges et Acieries de St. Etienne," the tensile strengths of two interesting series of nickel-carbon steels, which are reproduced in Table XXXIII. In both series the rolled bars were heated to a dull cherry red, and allowed to cool slowly in sand. In the steels containing 15 per cent. of nickel it will be noticed that, as the carbon is raised from 0·06 to 0·27 per cent., the ultimate stress is increased from 73·0 to 95·4 tons per square inch, but further increase in the carbon content brings about a progressive lowering of the tensile properties. With 25 per cent. of nickel the breaking load rapidly decreases as the carbon is raised from 0·05 to 0·26 per cent., and then remains almost constant as the carbon is raised to 0·83 per cent. Whilst no figures are given to indicate how much of the carbon is in the combined and how much in the graphitic condition, there can be no doubt that the action of the carbon is to lower the temperature of the transformation points. In discussing these figures, Osmond [1] said:—"When the transformations take place at temperatures higher than 400° C., they are almost completed and their effect was feeble.

---

[1] Discussion on Arnold's paper (*loc. cit.*).

When the transformations take place at temperatures lower than 400° they are more incomplete, and the steels are then hardened whatever t method of cooling. Lastly, steels which are not transformed at ordina temperatures possessed a characteristic combination of strength a plasticity."

TABLE XXXIII.

Nickel Constant = 15 per cent.			Nickel Constant = 25 per cent.		
Carbon.	Manganese.	Tensile Strength.	Carbon.	Manganese.	Tensile Strength.
Per cent.	Per cent.	Tons per square inch.	Per cent.	Per cent.	Tons per square inch
0·06	0·02	73·0	0·05	..	66·2
0·12	0·04	86·0	0·12	0·02	65·9
0·19	0·06	93·3	0·18	0·03	49·8
0·27	0·03	95·4	0·26	0·04	41·8
0·38	0·03	90·8	0·34	0·04	42·7
0·50	0·05	86·6	0·43	0·05	45·3
0·58	0·06	78·4	0·52	0·06	48·1
0·64	0·06	54·5	0·61	0·06	46·0
0·75	0·05	50·5	0·72	0·06	45·6
0·86	0·05	45·8	0·83	0·07	43·0

Hence, with 15 per cent. of nickel increasing the carbon to 0·27 per ce simply lowers the temperature of the inversion to that at which it has t greatest effect upon the hardening of the mass, whereas any further increa of carbon lowers it to such an extent that there is less and less internal worki of the steel. Or, in other words, when the transformation has been complet lowered to or below the ordinary temperature by sufficient nickel or nic plus carbon, the steel is in an unstressed or unworked condition. T corresponds to what is generally called γ-iron—*i.e.*, the material is in a sta austenitic state, and shows under the microscope the well-known polyhed crystal grains (see fig. 168). In this condition nickel steels are soft. Wh there is not so much nickel the steel becomes internally strained, or, L. Dumas[1] says, there arises a "working effect," which evinces itself b progressive increase in the elastic limit and ultimate stress. The extent this internal working, which is indicated by the martensitic markings, depe upon the amount of nickel, etc., present, the maximum effort being evid with about 14·0 per cent. when no carbon is present.

In a noteworthy paper dealing with the "Steel used for Motor-Car C struction in France," Dr. Guillet[2] draws attention to many important ap cations of nickel steel, and he published these in such a condensed fo that they are introduced here in detail:—

"It may be necessary for me to revert briefly to the investigations wh I have made on nickel steels, and which have been from time to time p lished elsewhere.[1] I have shown that, from the point of view of their microstructure, nickel steels can be divided into three well-defined classes—pearlitic steels, martensitic steels, and γ steels; that there is an intimate relation between the constitution and the mechanical properties of a steel, and that, finally, the determination of the transformation of one group into another depends essentially on the sum of C + Ni. Combining all my results, I have been able to form an exceedingly simple diagram. The percentage of carbon being indicated on the axis x, and that of nickel on the axis y, three zones can be distinguished, corresponding to the three constituents, and, further, to the zones of transformation.

---

[1] *Journ. Iron and Steel Inst.* 1904.

[2] *Journ. Iron and Steel Inst.*, 1906, No. 1.

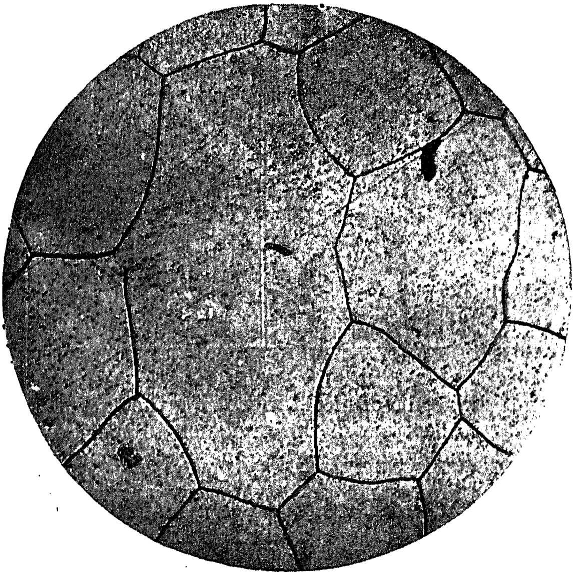


Fig. 168.—Austenite (*Carpenter*). × 1,000.

"It may be recalled that martensite is characteristic of a steel having been quenched at a suitable temperature. If we take a steel with 0·12 per cent. of carbon and 7 per cent. of nickel, it will be found to be pearlitic. Let it undergo cementation, so that the exterior may contain 0·90 to 1·0 per cent.; we shall then have the exterior consisting of martensite, and, consequently, having the same structure as a quenched case-hardened steel. To summarise: starting with a steel containing 7 per cent. of nickel alone, to obtain the same results as by case-hardening followed by quenching. We will not dwell on the importance of this process which, both in France and elsewhere, is carried out under the licence of the Dion-Bouton Company.

"By observing the necessary precautions, and, in particular, by annealing the steel on its arrival from the mill to destroy hammer hardening, and by taking care to allow the cemented pieces to cool as slowly as possible, it becomes possible to avoid all the worries which accompany quenching, and consequently all the operations which should follow it—*i.e.*, straightening and readjusting.

---

[1] *Bulletin de la Société d'encouragement pour l'Industrie Nationale*, and *Les Aciers Spéciaux*, Paris: Vve. Dunod.

"It must be further noted that this steel (carbon, 0·12; nickel, 7·0 per cent.) possesses certain very interesting mechanical properties in the annealed state, and that these properties are not changed on case-hardening. Its mechanical properties are:—

Tensile strength,	35 to 38 tons.
Elastic limit,	25½ to 28½ tons.
Elongation,	30 to 25 per cent.

"The motor-car parts which are most usually case-hardened are axles, particularly for single-cylinder cars, and crank-shafts, in regard to which the serious deformations which occur render it desirable to avoid the operations of case-hardening and quenching; the gearing, or at least such of it as is subjected to much work, and, generally speaking, all parts that have to undergo friction, and are not liable to any risk of shock.

"B. *Steels with Low Nickel* (1 *to* 6 *per cent.*), *and Medium Carbon* (0·25 *to* 0·4 *per cent.*).

"These steels are employed chiefly for shafts, forgings, axle journals, and axles, bearings, and various sections. The principal types are:—

"1. Carbon, 0·3 to 0·4 per cent.; nickel, 1 to 2 per cent. This is practically the ordinary type of ordnance material as used in France. It gives—

Tensile strength,	31·75 to 38 tons.
Elastic limit,	20 to 24 tons.
Elongation,	27 to 20 per cent.

"Quenched at 800° C. and annealed at 500° C., it gives—

Tensile strength,	44·5 to 57 tons.
Elastic limit,	35 to 47 tons.
Elongation,	16 to 12 per cent.

"2. Carbon, 0·20 to 0·25 per cent.; nickel, 3·25 to 3·50 per cent. This steel is used specially for journals. It gives—

Tensile strength,	35 to 41 tons.
Elastic limit,	21½ to 25½ tons.
Elongation,	25 to 20 per cent.

"Quenched at 800° C. and annealed at 500° C., it gives—

Tensile strength,	54 to 66 tons.
Elastic limit,	42 to 54½ tons.
Elongation,	11 to 14 per cent.

" 3. Carbon, 0·20 per cent.; nickel, 5 to 6 per cent. This steel is used, more particularly, for axles and axle boxes, and, after annealing at 900° C. and slow cooling, gives—

Tensile strength, ...	38 to 44½ tons.
Elastic limit, ...	23 to 26½ tons.
Elongation, ...	25 to 20 per cent.

" The properties of this steel undergo considerable modification on quenching. Quenched in water from a temperature of 850° C., it gives—

Tensile strength, ...	70 to 85 tons.
Elastic limit, ...	60 to 70 tons.
Elongation, ...	6 to 10 per cent.

" All the nickel steels of which mention has been made are pearlitic steels —that is to say, they have the same structure as ordinary carbon steels and, according to all the investigations made, it would seem that the iron was in a state of solution in the nickel. The advantages which these steels present over ordinary nickel steels are as follows:—Homogeneity; higher tensile strength and elastic limit, which is higher than that of an ordinary carbon steel, the higher the percentage of nickel present; an elongation which is uniformly high; very high resistance to shock (144 to 325 foot-pounds on annealed notched bars), and a considerable increase in tensile strength on quenching in water.

" C. *Steels with a Medium Percentage of Nickel* (10 *to* 18 *per cent.*).

" These steels have a medium percentage of carbon (0·20 to 0·50 per cent.).

" I have shown that all these steels are martensitic—that is to say, that they are very hard to work, very difficult to forge, etc. There are, therefore, strong objections to their employment, and they have consequently been almost entirely superseded.

" It may, however, be stated that an important French works still continues the manufacture of a nickel steel containing 16 to 18 per cent. of nickel. This steel gives—

Tensile strength, ...	63½ to 64½ tons.
Elastic limit, ...	58½ to 60 tons.
Elongation, ...	6 to 8 per cent.

" Nickel steels containing over 15 per cent. of nickel and over 0·25 per cent. of carbon soften slightly on prolonged annealing in the vicinity of 700° C., and can have their hardness restored on quenching in air, in the vicinity of 800° C.

" To sum up, these steels are all sub-martensitic, and present such difficulties to utilisation and working that, practically, their use has been abandoned.

" D. *Steels with a High Percentage of Nickel* (32 *to* 36 *per cent.*) *and a Low Percentage of Carbon* (0·12 *to* 0·20 *per cent.*).

" These products have found, in the motor-car industry, an important application in the making of valves. They contain at least 32 per cent. of nickel; with a lower percentage they would be susceptible of undergoing the most injurious transformations, of which I shall have occasion to refer to later.

" These high nickel steels are steels containing γ iron; their characteristics are the possession of a low elastic limit, high elongation, and a highly remarkable degree of resistance to shock. In addition to this they are untarnishable.

" These steels give—

Tensile strength, ...	38 to 44½ tons.
Elastic limit, ...	19 to 25½ tons.
Elongation, ...	40 to 30 per cent.

" Shock tests on notched bars gave 325 to 361 foot-pounds. Quenching perceptibly softens them, as it also does, by the way, all steels containing γ iron. On quenching they give—

Tensile strength, ...	33 to 38 tons.
Elastic limit, ...	14 to 19 tons.
Elongation, ...	50 to 40 per cent.

" It may not be inopportune to recall the fact that these steels were made the subject of a highly important study by Guillaume. This scientist showed, in particular, that the steel containing 36 per cent. of nickel possessed an exceedingly small coefficient of dilatation between the temperature of 0° C. and 350° C.

" E. *Steels with High Percentages of Nickel* (25 *to* 30 *per cent.*) *and High Percentages of Carbon* (0·60 *to* 0·80 *per cent.*).

" These steels have, for some time past, been used for crank-shafts, valves, etc. They possess, however, certain serious disadvantages which I will here indicate. It may be stated, to begin with, that they are γ steels, and accordingly possess low elastic limits. Further, these steels undergo, in the process of working (hammer hardening), annealing, quenching, etc.—conditions some of which very frequently occur in practice, particularly in making valves which require to be subjected to certain temperatures—well-marked intermolecular transformations; the γ iron is transformed into martensite.

" I will instance some examples from the point of view of the alterations they undergo in their mechanical properties."

TABLE XXXIV.—Steel with 0·80 per cent. of Carbon and 25 per cent. of Nickel (*Guillet*).

	Tensile Strength.	Elastic Limit.	Elongation.	Shock Tests.
	Tons.	Tons.	Per cent.	Kgm.
Annealed for 10 minutes at 900° C.,	45¾	24¼	33	35
Annealed 1 hour at 900° C., . .	54	30¾	10	12
Annealed 4 hours at 900° C., . .	58¼	34¼	6	8
Hammered and annealed for 10 minutes at 900° C., ...	55¾	28	11·5	10
Cooled to − 180° and reheated to 20° C., ...	61	38½	8	8

Guillet also mentions another case which is of particular interest, in so much as it clearly manifests the combined action of nickel and carbon in a most striking and useful manner. A steel containing 0·12 per cent. of carbon and 7 per cent. of nickel, as slowly cooled, contains its carbon in the pearlitic form. If this steel is subjected to the cementation process until the outside surface contains about 0·9 per cent. of carbon, followed by slow cooling, the surface will be in the martensitic state, and will consequently be hard. Thus, simply by carburising a steel of this composition, it is possible to obtain the same results as the, carburising and quenching, case-hardening of ordinary carbon steels. Hence, as Guillet says, "it becomes possible to avoid all the worries which accompany quenching, and consequently all the operations which should follow it—*i.e.*, straightening and readjusting."

TABLE XXXV.

Analysis per Cent.						Limit of Elasticity in Tons per Square Inch.		Breaking Load in Tons per Sq. Inch on Original Area.		Total Elongation per Cent. on 2 Inches.		Reduction of Area per Cent.		Appearance of Fractured Test Bar.
Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Tungsten.	Unannealed.	Annealed.	Unannealed.	Annealed.	Unannealed.	Annealed.	Unannealed.	Annealed.	
0·13	0·03	0·12	0·06	0·22	0·10	20·00	14·50	25·50	22·50	35·30	43·10	60·74	65·46	Dark granular; fibrous and silky.
0·15	0·04	..	..	0·22	0·20	22·50	16·50	27·50	22·50	40·85	46·30	60·74	66·48	Granular; fibrous; silky at edges.
0·15	0·07	0·10	0·08	0·29	0·40	24·00	18·00	31·00	25·50	33·00	39·60	59·80	60·10	Granular; fibrous; silky.
0·13	0·04	..	..	0·18	0·35	20·00	16·50	27·50	23·00	37·35	44·95	58·34	68·90	Granular; fibrous; silky at edges.
0·21	0·05	..	..	0·18	0·81	29·00	18·00	32·25	26·25	35·28	37·60	63·36	53·26	Dark granular; fibrous; silky.
0·22	0·05	..	..	0·18	1·20	25·00	17·50	32·50	27·00	25·75	37·68	49·34	54·38	Dark granular; fibrous and silky.
0·21	0·07	0·12	0·07	0·25	1·49	20·00	19·50	34·50	28·50	26·35	36·90	46·72	54·88	Granular; fibrous; silky at edges.
0·28	0·06	0·10	0·06	0·28	3·40	31·00	23·00	41·00	34·00	29·50	33·90	51·80	53·02	Granular; fibrous; silky at edges.
0·38	0·11	..	..	0·20	7·47	37·50	24·00	63·00	40·00	14·15	25·65	18·42	38·46	Very fine dark crystalline, with dark spot at edge from which fracture radiates.
0·46	0·08	..	0·06	0·28	8·33	45·00	25·50	64·00	42·50	2·50	22·80	2·48	32·62	Fine crystalline with small defect at edge.
0·63	0·10	..	..	0·25	10·56	55·00	28·50	80·00	48·00	5·19	10·00	4·80	10·24	Very fine dark crystalline.
0·76	0·19	..	..	0·28	15·65	Too hard to machine in unannealed condition.	27·50		57·00		3·45		2·56	..
						Bar had								

TABLE XXXVI.—Tensile Tests.

Mark.	Analysis.		Elastic Limit.	Maximum Stress.	Elongation per cent. on 2 Inches.	Reduction of Area.	Remarks on Fracture.
	C per cent.	W per cent.	Tons per sq. inch.	Tons per sq. inch.		Per cent.	
924 N	0·144	3·25	24·44	34·27	28·5	62·8	Dull grey granular, cup and cone with deep silky edges.
922 N	0·218	3·24	25·27	33·19	27·5	61·0	Very similar to 924 N.
923 N	0·27	2·92	29·0	39·3	24·1	59·8	Similar to foregoing.
921 N	0·48	3·11	41·54	53·75	16·0	45·5	Still granular with silky edges.
981 N	0·53	3·18	45·08	55·82	16·0	47·9	Rather lighter, but still granular.
920 N	0·57	3·17	44·56	57·76	14·5	44·2	As 981 N.
965 N	0·89	3·08	48·87	62·00	13·5	29·5	Extremely finely crystalline. Flatter, but still traces of silky edges.
964 N	1·07	3·09	40·37	50·82	15·5	28·2	Very finely crystalline. Flat.
719 N	1·24	3·02	46·1	56·0	9·5	16·9	Very finely crystalline.

CHAPTER XVII.

TUNGSTEN CARBON-STEELS.

THE metal tungsten is used as a special element in steels for permanent magnets, cold chisels, the old self-hardening Mushet tool steel, and the modern types of high-speed cutting tools.

Valuable information relating to the physical and mechanical properties, and the chemical and structural constitution of these steels, has been published by Sir Robert Hadfield,[1] Mr. Osmond,[2] Dr. Guillet,[3] Otto Böhler,[4] Dr. Swinden,[5] Professors Arnold and Read,[6] and others. Indirect evidence has also been supplied by Professor Carpenter [7] and the author.[8]

The data shown in Tables XXXV. and XXXVI. are taken from Hadfield's and Swinden's papers respectively. From Table XXXV. it will be observed that the elastic limit and tensile strength are comparatively low in all cases, and, as Hadfield says, the action of tungsten in this respect differs considerably from that of nickel, chromium, and manganese. The best all-round mechanical results appear to be obtained with 3·5 per cent. of tungsten.

The results obtained by Swinden from a series containing approximately 3·0 per cent. of tungsten with varying carbon content very clearly show the toughening effect of tungsten, particularly as the carbon increases. Compared with iron-carbon steels, the tenacity has been considerably raised, with only slight lowering of the ductility. The specimen with 0·89 per cent. of carbon gives remarkably good results, but with higher carbon content the mechanical properties are not so good.

The composition of steel which seems to be most generally preferred for permanent magnets is carbon about 0·6 per cent. and tungsten from 5 to 6 per cent. According to Dr. Swinden's [9] experiments upon the magnetic properties of tungsten steels, it would seem that the best results are obtained by quenching from about 900° C. This temperature is necessary, he says, in order to get the carbon into solution. Judging from the excellent discussion which took place on the above-mentioned paper, there does not appear to be any definite idea as to what is the real cause of the peculiar properties of permanent magnets. There is, however, no doubt that this property is materially influenced by the size of crystals contained in the mass, being better the finer the grain. Hence mechanical work is generally admitted to have a beneficial effect. In regard to the action of quenching, Arnold observes that "in iron containing 0·1 to 0·9 per cent. of carbon the permanent magnetism is directly proportional to the sub-carbide of iron present." In other words, hardenite alone holds permanent magnetism. It may, therefore, be found that the permanent magnetism of quenched steels is in some way connected with the internal working of the steel which is produced in the quenching operation.

---

[1] "Alloys of Iron and Tungsten," *Journ. Iron and Steel Inst.*, 1903, No. 2.

[2] *Journ. Iron and Steel Inst.*, 1890, No. 1.

[3] *Revue de Metallurgie*, 1904, p. 263.

[4] *Wolfram und Rapid Stahl*, 1903.

[5] "Carbon-Tungsten Steels," *Journ. Iron and Steel Inst.*, 1907, No. 1; and "The Constitution of Carbon-Tungsten Steels," *Journ. Iron and Steel Inst.*, 1909, No. 2.

[6] *Proc. Inst. Mech. Engs.*, 1914.

[7] *Journ. Iron and Steel Inst.*, 1905, No. 1.

[8] *Ibid.*, 1908, No. 2.

[9] "Magnetic Properties of Tungsten-Carbon Steels," *Proc. Inst. Elec. Engs.*, 1909, part 195, vol. xlii.

Constitution of Tungsten Steel.

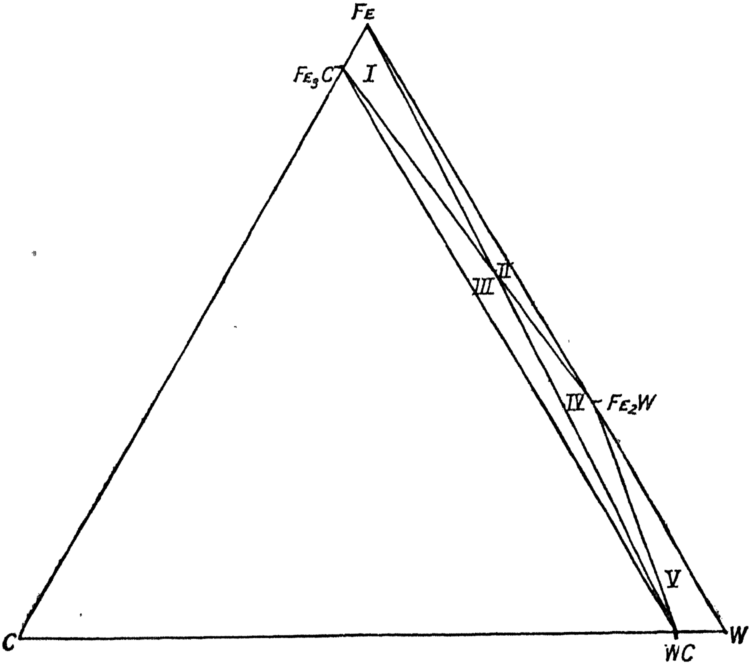
Osmond found in his early work that if annealed tungsten-carbon steels be heated to a temperature not exceeding about 900° C., the position of the carbide change point is not sensibly altered. It occurs at practically the same temperature as when pure carbon steels are cooled. This observation has been amply confirmed by all subsequent workers, and it may be noted that, even in the presence of 19·28 per cent. of tungsten and 0·63 per cent. of carbon, the temperature of the carbide change is still 700° C.

In the absence of any direct chemical or microscopical evidence to the contrary, this fact naturally led investigators to suppose that, even in the presence of such high percentages of tungsten, the carbon still remained in combination with the iron as Fe_3C, and gave rise to the same inversion. There is, however, now no doubt that this view is incorrect. Another interesting fact which was first brought forward by the above worker, is that the Ar_3 and Ar_2 points are practically uninfluenced by the tungsten contained in the steel. These changes take place at the same temperature in tungsten steels, as they do in carbon steels of the same carbon content, providing the initial temperature from which the former are cooled does not exceed about 1,040° C. But this treatment—*i.e.*, heating to 1,040° C.—produces a very sharp lowering of the carbide point in steels containing tungsten.

He also showed that, when the specimens were heated to 1,300° C., the Ar_3 and Ar_2 points are lowered in turn, and tend to meet the lowered carbide change, and, under certain conditions, the normal carbide change could be split—*i.e.*, part occurring at, say, 700° C. and part at the lower temperature.

The temperature of this low change appears to be directly related to the percentage of tungsten. With 3·0 per cent. of tungsten Swinden has fixed the low point at 570° C., and has indicated that with increasing carbon the initial temperature must be raised in order to lower the temperature of the normal carbide change. Though not experimenting under the same conditions, it would appear from the author's work that with about 18 per cent. of tungsten the temperature of the low change point is at 380° C. It is, therefore, evident from the above facts that the action of tungsten in many ways differs strikingly from most other elements in special steels. Far more complications are met with in the steels under consideration, and these make it much less easy to offer a trustworthy theory of the function of tungsten. Nevertheless, the careful separation of the chemical compounds existing in tungsten steels which has recently been effected by Professors Arnold and Read enable us to approach this difficult problem with much more confidence than was previously possible. They have shown that when the ratio of carbon to tungsten is 1 : 15·3 the whole of the carbon is in combination with the tungsten as WC. If the carbon is greater than this ratio mixtures of the two carbides, Fe_3C and WC, are present, and if the tungsten is in excess there is no carbide of iron, but a mixture of carbide of tungsten, WC, and a tungstide of iron, Fe_2W.

At this stage it should also be noted that Swinden obtained evidence which certainly indicates that a compound having the empirical formula Fe_3W separates from liquid tungsten-iron alloys which contain high percentages of tungsten. In view of Arnold and Read's work, it would seem that this compound does not exist in annealed tungsten steels, it is probably broken up at a temperature below the solidus into Fe_2W and Fe. Be that as it may, we are now able to predict the condition of the carbon and tungsten contained in any annealed steel belonging to this class when the chemical composition is known.



I. = ferrite + Fe_3C + Fe_2W.
II. = ferrite + WC + Fe_2W.
III. = Fe_3C + WC + Fe_2W.
IV. = WC + Fe_2W + ?
V. = —

Fig. 169.

The diagram (fig. 169), which is based upon the above chemical evidence, represents the various areas of composition in which the carbides of iron and tungsten and the tungstide of iron and free iron exist, for all alloys which may be regarded as coming under the heading of steels. This alone is a substantial step towards a better understanding of the effect of tungsten upon the critical points occurring in these steels.

It has already been pointed out that tungsten alone has no influence upon the Ar_3, Ar_2, nor the carbide change providing a temperature of about 950° C. is not exceeded. This is true, even when as much as 19·0 per cent. of that element is present. Since with this quantity of tungsten and only 0·63 per cent. of carbon present no carbide of iron can exist, it is quite obvious that the carbide change at about 700° C. must be attributed to the deposition of tungsten carbide WC, and not to carbide of iron. It may at first sight seem rather remarkable that the carbide WC should be deposited at practically the same temperature as Fe_3C, but this is not so strange when it is remembered that the empirical formulæ for the two compounds indicate that they have very similar molecular weights—viz., $Fe_3C = 179 \cdot 2$ and $WC = 196 \cdot 0$. Hence, considered from a purely physico-chemical standpoint, the observed effect of tungsten carbide upon the critical points of iron—when cooled from temperatures not exceeding 1,000° C.—is precisely what might have been anticipated. For example, if there is any connection between the known physical law relating to the molecular lowering effect of salts upon the freezing points of liquids, and the effect of elements upon the transformations in metallic alloys, then compounds such as Fe_3C and WC, possessing almost the same molecular weights, will produce similar physico-chemical effects. Naturally, great care must be exercised in considering a view of this kind, because so much depends upon the solubility of the compound in the constituents or phases which are formed at the lower temperature, but in the case of iron-carbon and iron-carbon-tungsten steels the solubility of their respective carbides appears to be almost negligible. It is also interesting to note that the experimental work which has been done indicates that tungsten has little, if any, influence upon the carbon content of the eutectoid steel.

As regards the lowering of the carbide change, which is produced by heating tungsten steels above 1,000° C., and which is the real cause of the self-hardening properties of these alloys, it must be admitted that there is no direct evidence to show exactly what happens at those high temperatures. There is every reason to believe that when the tungstide Fe_2W is present, it progressively goes into solution as the temperature is raised above 800° C. The temperature at which this is completely effected depends upon the amount of compound present being higher as the tungstide is increased. When in solution the temperature of the carbide change is lowered on cooling, but it is perhaps an open question whether this lowering is purely due to the Fe_2W in solution or whether some chemical change also occurs. At temperatures above 1,000° C. there may be a chemical reaction between the iron and tungsten carbide which gives rise to a new compound resulting in the disappearance of the critical point at 700° C., and the appearance of another point at lower temperatures. In support of this, a steel containing 1·07 per cent. of carbon and 3·09 per cent. of tungsten, in which there should be no free tungstide of iron gives the same lowering of the carbide change after heating to high temperatures.

which may be regarded as coming under the heading of steels. This alone is a substantial step towards a better understanding of the effect of tungsten upon the critical points occurring in these steels.

It has already been pointed out that tungsten alone has no influence upon the Ar_3, Ar_2, nor the carbide change providing a temperature of about 950° C. is not exceeded. This is true, even when as much as 19·0 per cent. of that element is present. Since with this quantity of tungsten and only 0·63 per cent. of carbon present no carbide of iron can exist, it is quite obvious that the carbide change at about 700° C. must be attributed to the deposition of tungsten carbide WC, and not to carbide of iron. It may at first sight seem rather remarkable that the carbide WC should be deposited at practically the same temperature as Fe_3C, but this is not so strange when it is remembered that the empirical formulæ for the two compounds indicate that they have very similar molecular weights—viz., $Fe_3C = 179 \cdot 2$ and $WC = 196 \cdot 0$. Hence, considered from a purely physico-chemical standpoint, the observed effect of tungsten carbide upon the critical points of iron—when cooled from temperatures not exceeding 1,000° C.—is precisely what might have been anticipated. For example, if there is any connection between the known physical law relating to the molecular lowering effect of salts upon the freezing points of liquids, and the effect of elements upon the transformations in metallic alloys, then compounds such as Fe_3C and WC, possessing almost the same molecular weights, will produce similar physico-chemical effects. Naturally, great care must be exercised in considering a view of this kind, because so much depends upon the solubility of the compound in the constituents or phases which are formed at the lower temperature, but in the case of iron-carbon and iron-carbon-tungsten steels the solubility of their respective carbides appears to be almost negligible. It is also interesting to note that the experimental work which has been done indicates that tungsten has little, if any, influence upon the carbon content of the eutectoid steel.

As regards the lowering of the carbide change, which is produced by heating tungsten steels above 1,000° C., and which is the real cause of the self-hardening properties of these alloys, it must be admitted that there is no direct evidence to show exactly what happens at those high temperatures. There is every reason to believe that when the tungstide Fe_2W is present, it progressively goes into solution as the temperature is raised above 800° C. The temperature at which this is completely effected depends upon the amount of compound present being higher as the tungstide is increased. When in solution the temperature of the carbide change is lowered on cooling, but it is perhaps an open question whether this lowering is purely due to the Fe_2W in solution or whether some chemical change also occurs. At temperatures above 1,000° C. there may be a chemical reaction between the iron and tungsten carbide which gives rise to a new compound resulting in the disappearance of the critical point at 700° C., and the appearance of another point at lower temperatures. In support of this, a steel containing 1·07 per cent. of carbon and 3·09 per cent. of tungsten, in which there should be no free tungstide of iron gives the same lowering of the carbide change after heating to high temperatures.

CHAPTER XVIII.

HIGH-SPEED TOOL STEELS.

As an introduction to the development and use of high-speed tool steel, the following quotation from a paper by Mr. J. M. Gledhill [1] may be given. He says:—"It would doubtless have been felt by many but a few years ago that there was little left to be said on the subject of crucible tool steel, and that something akin to finality had been arrived at in its manufacture and general treatment. Probably such feeling was justifiable, when it is remembered that the making of steel in crucibles is by far the oldest method known, dating back from time immemorial, it being indeed impossible accurately to trace its origin and earliest development, but it seems certain that carbon steel was made and used thousands of years ago for cutting tools. Proof of this may be seen by the marvellous carvings and workings on the intensely hard stone work of the ancients, for it would be difficult to conceive by what means, other than with steel tools, such work could have been executed, and it is wonderful that steel-cutting tools should have been used so long ago. Archæologists have discovered that the Chinese made steel in crucibles long before the Christian era. 'Wootz' steel, fabricated in India centuries ago, was crucible steel, as also was the celebrated Damascus steel, produced at the forges of Toledo, and curiously enough this latter steel furnishes yet another proof that 'there is nothing new under the sun,' for it has been recorded that Damascus steel contained certain percentages of tungsten, nickel, manganese, etc., some of the very elements, in fact, contained in the present modern high-speed steels, so that a latent high-speed steel may be said to have existed centuries ago, and all that was necessary to bring out its inherent powers would have been the heating of it in a 'paradoxical' manner, so to speak—that is, to such a high temperature as was long thought would impair or destroy the nature of such steel."

The era of ordinary carbon steel for cutting purposes is generally considered to extend up to some time between 1860 and 1870, when Robert Mushet succeeded in making tungsten steel. He discovered that, with fairly large percentages of tungsten, along with more manganese than had been previously used, and carbon in tool steel, conferred on the material the peculiar property of being nearly as hard after it was slowly cooled in air from 1,000° C. as carbon steels were after they had been water-quenched. For this reason, Mushet steel became known as "self-hardening" or "air-hardening" steel. Moreover, in addition to this "self-hardening" property, he also found that tools made from tungsten steel also had the power of cutting at much higher speeds and would work for a longer time than carbon steels.

For some considerable time Mushet steel was regarded by engineers as a kind of metallurgical curiosity, and was not very widely used until about 1890, when it became recognised that its superior cutting powers more than compensated for the extra cost. Mushet steel did not hold the premier position as a tool steel for very long, because an even more remarkable advance was made in America by Messrs. Taylor and White, who developed what became known as high-speed cutting steel. Their first invention consisted in increasing the percentage of tungsten and introducing about 4·0 per cent. of chromium into the steel, and at the Paris Exhibition (1900) they gave public demonstrations of what were then considered to be astonishing results in the cutting speeds of tools. Since then the same investigators have made further improvements in the composition of this kind of steel, and an even greater advance in their heat treatment. They found that the cutting efficiency of all self-hardening steels is very substantially raised when they are hardened by heating the nose or cutting end of the tool to very near its melting point—*i.e.*, about 1,300° C. The compositions and relative cutting values of four kinds of steels, which are typical of the four different eras through which we have passed, are given in the following table, which has been taken from Mr. F. W. Taylor's paper.[1] :—

---

[1] *Iron and Steel Inst.*, 1904, No. 2.

TABLE XXXVII.

Make of Steel.	Carbon.	Silicon.	Manganese	Tungsten.	Chromium	Vanadium.	Speed per Minute Cutting Medium Steel.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Feet.
Jessop,	1·047	0·206	0·189	..	0·207	..	16
Mushet self-hardening,	2·15	1·044	1·578	5·441	0·398	..	26
Original Taylor-White,	1·85	0·15	0·30	8·00	3·80	..	58-61
Best modern high-speed (1906),	0·67	0·043	0·11	18·91	5·47	0·29	100

Mr. Taylor's valuable paper contains a store of useful information obtained from experiments that extended over a period of 25 years, and should be carefully studied by those interested in this subject. On p. 190 he says :—"Our experiments resulted in the following important discoveries :—(*a*) That, comparing the self-hardening steel with carbon steel, a gain in speed of 41 per cent. to 47 per cent. could be made in cutting a hard forging of about the quality of tyre steel, whereas a gain of nearly 90 per cent. could be made in cutting the softer qualities of metal ; and (*b*) that by using a heavy stream of water on the nose of a Mushet or other self-hardening tool, a gain of about 30 per cent. could be made in the cutting speed. These experiments, then, indicated clearly that the use of Mushet steel almost exclusively for cutting exceedingly hard pieces of metal was the wrong one, since an enormously greater quantity of soft metal was cut in the average machine shop than of hard metal, and the gain in cutting soft metals was 90 per cent. as against only 45 per cent. for hard. It thus became evident that, instead of usin self-hardening tools only occasionally for cutting extra hard pieces of meta they should be used daily throughout the shop on all ordinary work in plac of the ordinary carbon steel tools. From 1900 up to the present time may b called the era of high-speed tools, and this has become so completely the cas that at the present time a carbon or an 'untreated' tungsten-manganes or tungsten-chromium roughing tool can scarcely be found in an up-to-dat machine shop." There is no doubt that the most important discover made in connection with high-speed steels, is that which is due to Messr Taylor and White, relating to the high heat treatment. This may be applie to any tool steel containing not less than 0·5 per cent. of chromium and no less than 1·0 per cent. of tungsten or its equivalent. This treatment, whic

---

[1] *The Amer. Soc. of Mech. Engrs.*, 1906, vol. xxviii., pp. 31-350.

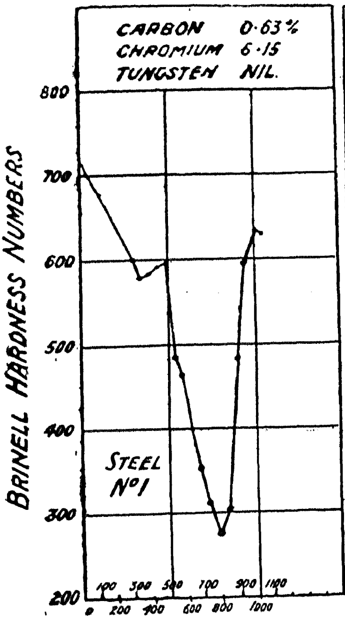


Fig. 170.

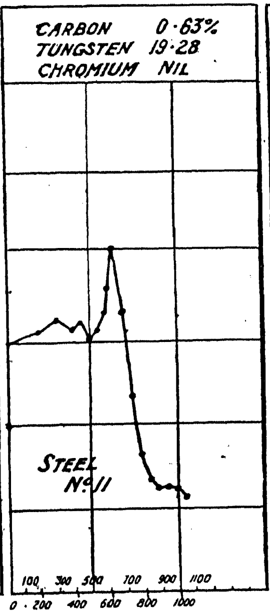


Fig. 171.

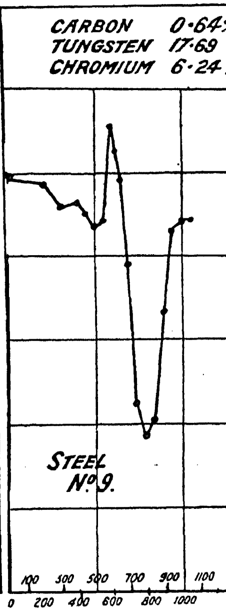


Fig. 172.

would completely ruin ordinary tools, imparts the new quality or proper which Taylor has described as "red-hardness," and it is this property whi enables these tools to run at their high cutting speeds.

Taylor distinguishes between the property of "hardness" and th of "red-hardness," and points out that heating chromium-tungsten ste close to their melting point does not give them a greater degree of hardn than quenched carbon steels, but it gives them the power of retaining wl hardness they have, even after the tool has been heated up to a red he In use, high-speed tools maintain their hardness and cutting edge, even af the nose of the tools and that part of the turnings which is exposed to t friction become red hot. As is well known, the hardness of ordinary carb steel tools is, practically speaking, entirely removed at about 350° C.

tempering. With high-speed steels, however, tempering up to 600° C. very materially increases their hardness.

The effect of heating a hardened steel containing 0·63 per cent. of carbon and 19·28 per cent. of tungsten is shown, diagrammatically, in Fig. 171. With the exception of the absence of chromium this material is typical of a high-speed steel. In this instance it will be observed that the Brinell hardness of the steel after hardening in an air blast from about 1,300° C. is only 500, but that this value does not fall after the material has been heated to temperatures up to 500° C. Further, by increasing the secondary heating to a little over 600° C. a marked increase in the hardness takes place, and reaches a value which is much greater than it was when first hardened.

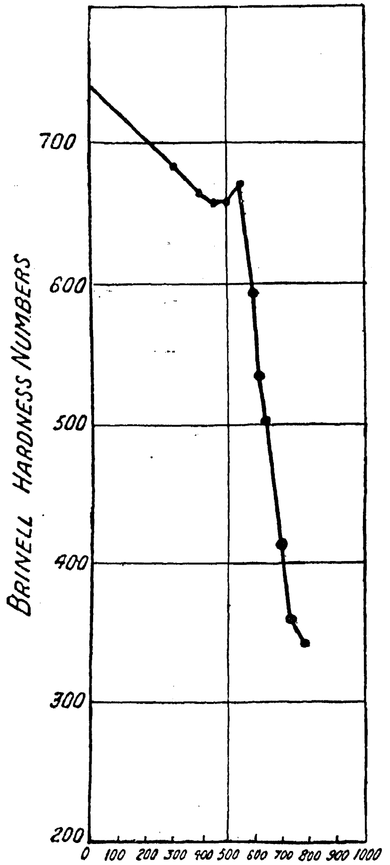


Fig. 173.—Tempering Temperatures °C.

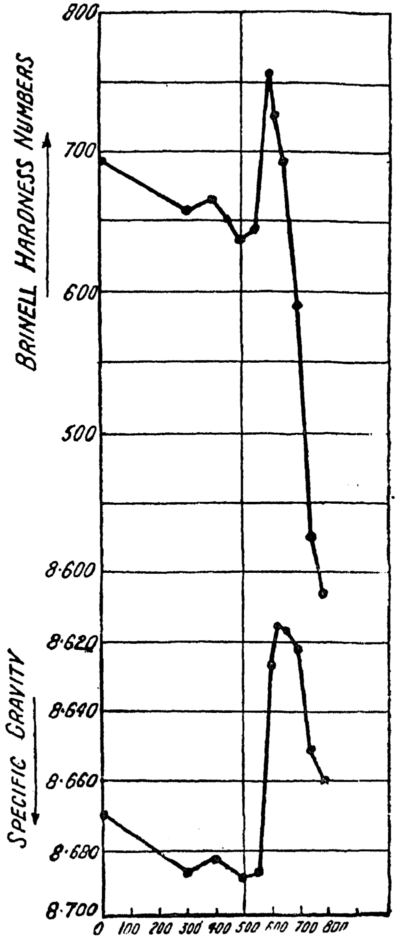


Fig. 174.—Tempering Temperatures °C.

With a steel containing 6·0 per cent. of chromium and 0·63 per cent. of carbon, Fig. 170, the Brinell hardness falls from above 700 to well below 600° after the hardened metal has been heated to 300° C. Between 300° and 500° becomes a little higher than it was after being heated to 300° C. With temperatures above 500° C. there is a rapid fall in the Brinell hardness.

With a steel containing 18 per cent. of tungsten, 6·0 per cent. of chromium and 0·63 per cent. of carbon, the effect of reheating properly hardened samples is shown in Fig. 172. Here it will be seen that the steel is very hard in the air-hardened state, and that the hardness falls rather markedly as the reheating is raised to 500, but at 600° C. a substantial secondary hardening sets in which makes the material much harder than it was in the initially air-hardened condition.

The temperature from which high-speed steels are hardened is perhaps the most important in the treatment of this class of steel. Broadly speaking, this should be practically as high as possible, short of actually melting the metal. This is very clearly represented in Fig. 173, which shows the influence of reheating samples of the same high-speed steel referred to above, that were hardened from 1,050° C. In this instance it will be noted that the steel loses its hardness more quickly than if it had been hardened from 1,300° C., and, further, it does not show anything like the same degree of secondary hardening. The difference in this respect is due entirely to the fact that the tungsten in these steels does not completely go into solution until temperatures approaching 1,300° C. are attained; and since it is to this element when in solution that we owe the secondary hardening and the power of retaining hardness at high temperatures, little or no return is obtained from that costly element unless the tool is heated to a high temperature prior to hardening.

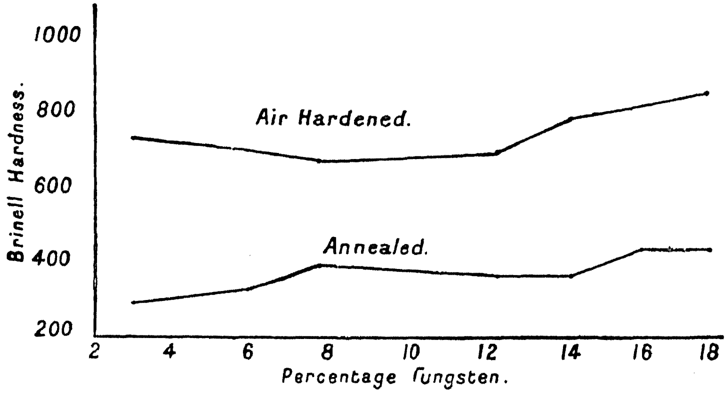


Fig. 175.

Experiments have been made to determine the variations in the specific gravity of high-speed steel after being air-hardened and tempered at different temperatures. A series of the results are plotted in Fig. 174 along with the hardnesses. A change in the hardness is apparently always accompanied with a corresponding alteration in the volume. Thus, with each increase of hardness there is an increase of volume.

The effect of varying quantities of chromium and tungsten upon the hardness of annealed and hardened tool steel is shown in figs. 175 and 176. The cutting properties of the same steels given in cutting speeds of feet per minute are also shown in figs. 177 and 178.

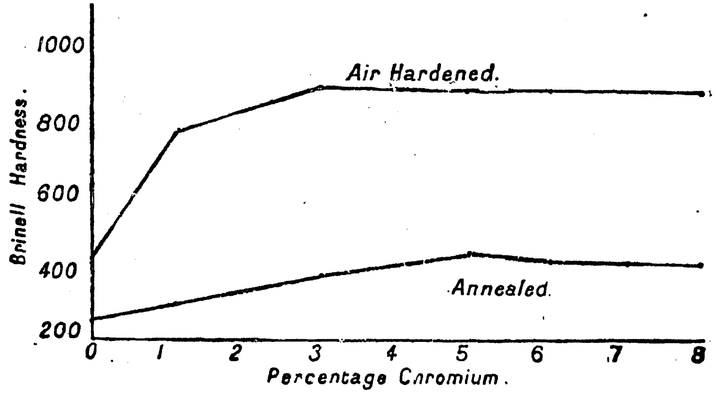


Fig. 176.

Molybdenum, which imparts a self-hardening effect upon steel similar to that of tungsten, was originally used in high-speed steels, but for some unknown reasons it did not give such good results, and it is now little used. Cobalt has the same effect, and tool steels containing 15·0 per cent. of this element are now in use, but practically no data have been published respecting them.

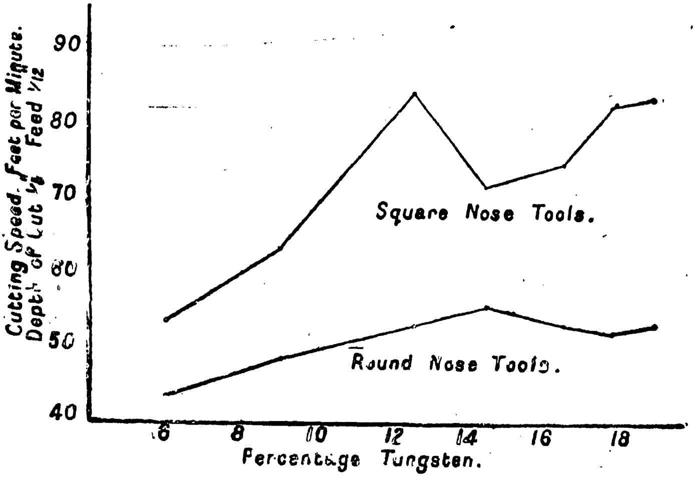


Fig. 177.

Small quantities of vanadium very materially improve the cutting properties of high-speed steels; 0·15 to 0·35 are said to be as effective as higher percentages. It is generally considered that the action of this element is that of a cleanser of the molten steel, because it frequently happens that when the above quantities are used, its presence cannot be detected in the finished material, but its beneficial effects are, nevertheless, evident. In all probability vanadium degasifies the molten metal by direct combination with the oxides and nitrides present, or in some way neutralises their injurious effects, such, for example, as rendering them more soluble and preventing them being evolved at the time the mass is solidifying in the mould. Investigations relating to the function of the various elements contained in modern high-speed steels have been made by Messrs. Böhler,[1] Osmond,[2] Le Chatelier,[3] Taylor and White,[4] Carpenter,[5] and the author.[6]

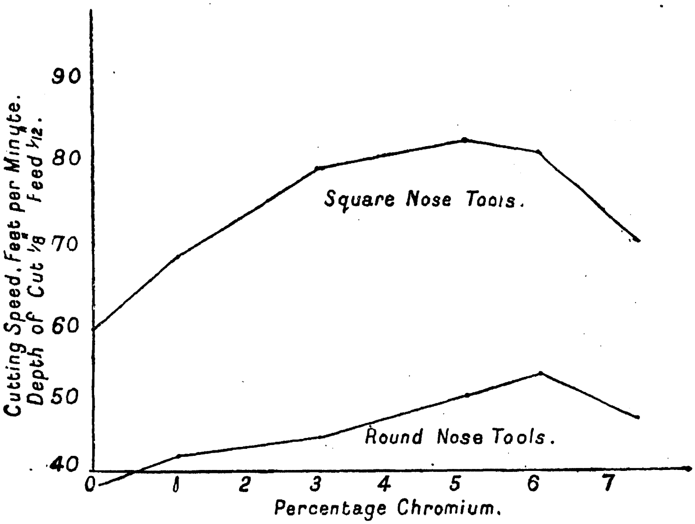


Fig. 178.

Böhler found that a steel containing 0·85 per cent. of carbon and 7·78 per cent. of tungsten possessed only one critical point at 700° C., if it had not been heated to above 1,000° C., but a second point appeared at 550° C. on cooling, if the initial temperature was higher than 1,000° C. When cooled from temperatures between 1,000° and 1,100° C. both these points existed, but the point at 700° C. disappeared if the cooling began from above 1100° C. He considered that both these critical points were due to what may be termed the carbide change—*i.e.*, the temperature at which the carbon separates from the γ-iron solid solution—and that the low point was merely the lower limit of the change which was depressed by the retarding action of the tungsten present. He also found that, as the percentage of tungsten was increased, it was necessary to heat to a higher temperature in order to bring about a splitting of the carbide change, and under these conditions the temperature of the low change was further depressed.

---

[1] *Wolfram und Rapid Stahl*, 1903.
[2] *Revue de Metallurgie*, 1904.
[3] *Ibid.*
[4] *American Society of Engrs.*, 1906.
[5] *Iron and Steel Inst.*, 1905, No. 1, and 1906, No. 2.
[6] *Ibid.*, 1908, No. 2.

He experimented with one high-speed steel containing chromium and tungsten, and advanced the view that the chromium and tungsten present in high-speed steels lowered the whole of the pearlitic change below that of atmospheric temperatures. Thus, these steels become hardened even when slowly cooled from high temperatures, because the softening action which accompanies the separation of the carbide is avoided.

The view put forward by Osmond, and supported by Le Chatelier, was that the softening which occurs as a result of the change from hardening into pearlitic carbon, which takes place at 700° C. in pure carbon steels, is retarded by the presence of tungsten, chromium, molybdenum, etc., when the mass is cooled from sufficiently high temperatures, and that this change is lowered in proportion as the quantity of those elements is raised above the eutectoid composition.

As the result of many experiments on the heating and cooling curves of high-speed steels, Carpenter concluded that the action of tungsten or molybdenum consists in hindering under certain conditions, and in altogether preventing under suitably chosen ones, changes in iron-carbon alloys which would have for their result the softening of the material, and in addition these elements impart a remarkably high resistance to the tempering of the hardened tools. For example, the tempering of hardened carbon steels begins when they are heated to 200° C., whereas the heating curves obtained by Professor Carpenter indicate that tempering of high-speed steels does not begin below 500° to 600° C. He also found that the 700° C. or carbide change point takes place in all these steels if the initial temperature of cooling did not exceed 900° C. If the initial temperature was anything between 900 and 1,200, this point was split into two or more parts and spread over a range of temperature from about 700° C. to 300° C., molybdenum being more effective than tungsten in producing this split. To suppress completely the carbide change and produce the austenitic structure, which is hard and tough, he said, it is only necessary to subject the nose of the tool to a very mild quenching, which completes the hardening that the presence of tungsten or molybdenum has more or less advanced.

The author found that steels containing 6·0 per cent. of chromium and 18·0 per cent. of tungsten gave evidence of only one thermal change on cooling at about 380° C., when the initial temperature was not much above 1,200° C., and when cooled from about 1,300° C. no critical point whatever can be detected on slow cooling.

A series of heating and cooling curves of a typical modern high-speed steel is shown in fig. 179, wherein are clearly illustrated the positions of the thermal changes, as the heat-treatment is modified. Curve No. 1 shows the normal carbide change of the steel when cooled from between 900° to 950° C., whilst curve No. 2 is from the same steel when cooled from about 1,300° C., which shows that the carbide change has been completely suppressed. The effect of subsequently heating and cooling the same specimen can be seen in the remaining curves Nos. 3, 4, 5, 6, and 7, and the splitting of the carbide point is evident in No. 8. Considered in the light of these curves, it does not seem that the function of tungsten or tungsten along with chromium is that of a mere brake retarding or depressing the carbide, but that there is some change of a chemical nature which takes place when these steels are subjected to temperatures above 950° C. If the suppression of the critical point was merely due to the presence of tungsten and not to the change in chemical constitution, one would expect the change to occur at its normal temperature in curve No. 6 after heating to 900° C., since an initial temperature of 900° C. has no effect upon the carbide change.

Dr. Swinden has advanced the theory that in the annealed steels the tungsten exists as Fe_3W separated in the mass, and that at the lowering temperature this compound goes into solution, and that the carbide of iron exists as such in this solution. Then, when this condition is obtained the Fe_3W does not again separate until the low point is reached, and the separation of Fe_3C immediately follows.

The author expressed the view that a carbide of tungsten is formed at the lowering temperature, which is not deposited from solution until the low point is reached. In both these cases, however, it is assumed that the ordinary Ar_1 point at 700° C. is due to the separation of carbide of iron, Fe_3C. The results which have recently been published by Professors Arnold and Read cast very considerable doubt upon this view, because they have shown that, with the percentages of carbon and tungsten usually present in high-speed steels, the carbon is in combination with the tungsten and not with the iron (see Chapter XVII.).

Hence, before it is possible to say with any certainty what is the exact change that occurs when these steels are heated to above 1,000° C., much more work is required. It is, however, known that the hardening which is produced by heating to high temperatures followed by relatively very slow cooling is caused by the action of the tungsten which suppresses the carbide change, and, further, that the chromium contained in these steels increases the rate of wherever reaction occurs at the high temperature, and materially improves the cutting properties of the tools.

Microstructures.

Although the comparison of high-speed steels vary within very considerable limits, it is a very remarkable fact that their structures as seen under the microscope are almost identical. Thus, fig. 180 is the typical microstructure of annealed steels containing 0·65 per cent. of carbon with from 3·0 to 7·0 per cent. of chromium and from 0·0 to 18·5 per cent. of tungsten. All these steels show the same kind of granular pearlite, and no appreciable difference can be detected in any of them.

A typical structure of hardened high-speed steel is illustrated in fig. 181, which consists of austenitic polygonal crystals.

The effect of tungsten upon the structure of the hardened steels is clearly indicated in figs. 182, 183, 184, and 185, from which it will be seen that as the percentage of tungsten is lowered the acicular or martensitic markings increase.

It was shown by the author that when hardened high-speed steels are heated to about 650° C. a new and very brittle constituent is formed (fig. 186). It was suggested that high-speed tools fail when cutting at their maximum speed, not so much because they lose their hardness, but because this brittle constituent is then formed and renders the cutting edge of the tool incapable of standing up to the work. The structure of the lip surface of a tool after it had been cutting at its maximum speed is shown in fig. 187. It will be noticed that after this treatment the steel, which in the first place consisted almost entirely of polygonal austenitic crystals, has been almost completely converted into the martensitic structure. It may also be noted that inside the long white areas there are indications of the above-mentioned brittle constituent.

This transformation from the austenitic into the martensitic structure is particularly interesting, in view of what Mr. F. W. Taylor says about the second or low heat-treatment which he recommends. This treatment consists in reheating the hardened tool to a temperature of 600° to 670° C. After this heat-treatment the cutting properties of the tool are improved. He also says that if the tool is allowed even for a short space of time to rise in temperature beyond 670° C., its property of red hardness will be seriously impaired, and its cutting speed greatly reduced. The beneficial effect of the second heat-treatment can be produced by running the tool under the friction of the clip until the temperature of its nose has been raised to something below 670° C., after which the tool can be run at much higher cutting speeds than it would otherwise be capable of doing.

In view of the increased hardness which is produced by heating these steels up to temperatures of 600° C. (see fig. 174), this low heat-treatment now becomes easy to understand, but it would seem that the upper limit is at 600° C., because heating to slightly higher temperatures very materially reduces the hardness of the steels.

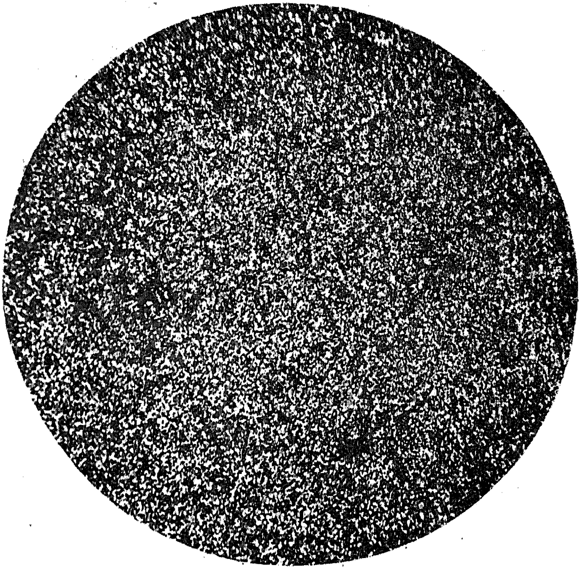


Fig. 180.—Typical Structure of Annealed High-Speed Steel. × 150.

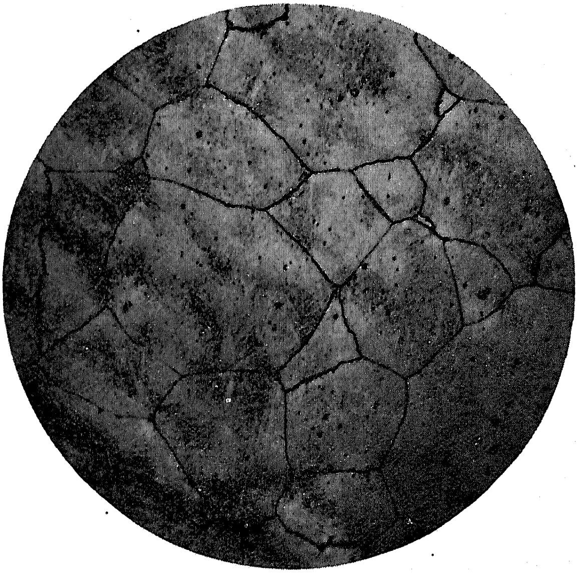


Fig. 181.—Typical Structure of Hardened High-Speed Tool Steel. × 1.000.

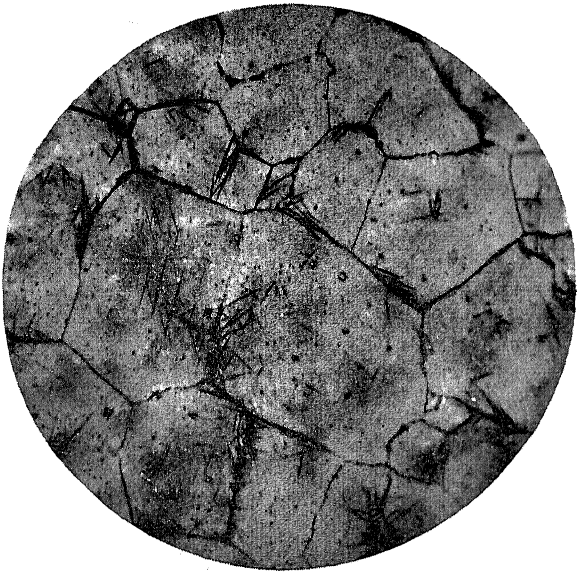


Fig. 182.—× 150.

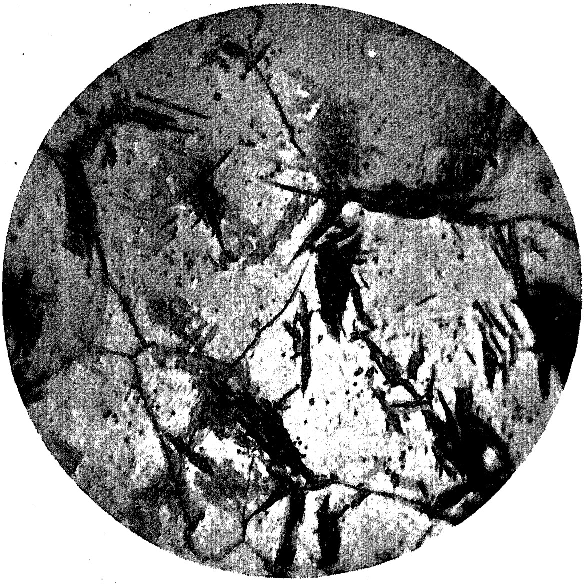


Fig. 183.—× 1,000.

Carbon,	·63 per cent.
Chromium,	6·00 „
Tungsten,	5·90 „

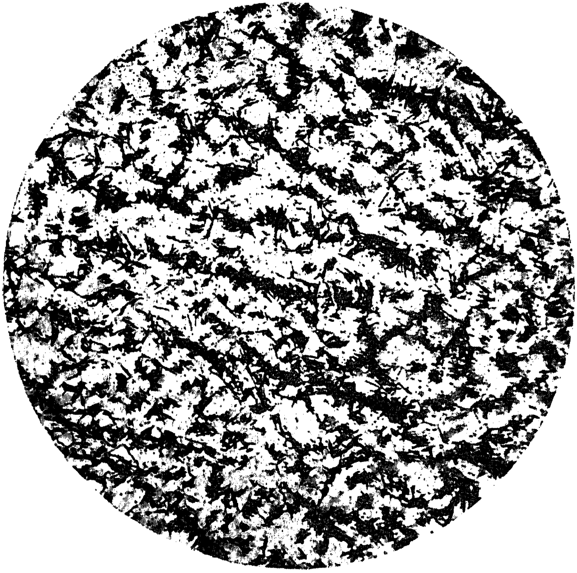


Fig. 184.—× 150.

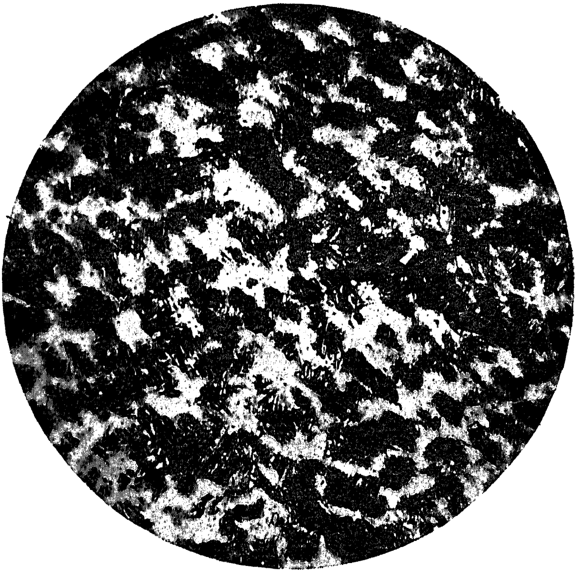


Fig. 185.—× 1,000.

Carbon, ...	·65 per cent.
Chromium, ...	6·0 ,,
Tungsten, ...	3·08 ,,

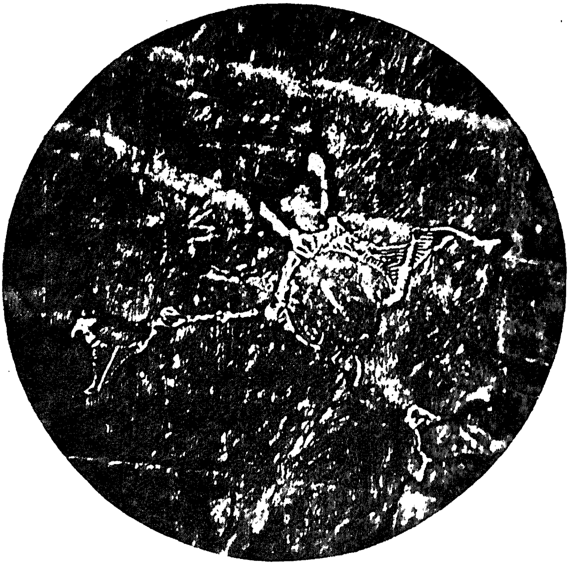


Fig. 186.—Tempered High-Speed Steel. × 1,000.

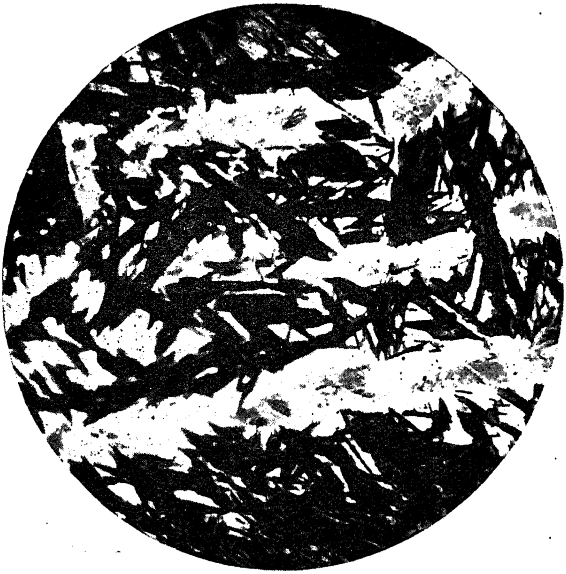


Fig. 187.—Structure of High-Speed Tool Steel after Cutting at its Maximum Speed for 20 Minutes.

CHAPTER XIX.

MANGANESE

The element manganese is extensively used in the metallurgy of steel. To ordinary steel it is usually added in the form of spiegel, in the bath, or later, as ferro-manganese, after the metal has been refined and tapped into the casting ladles. The two principal reasons for making this addition are, first, to reduce any oxides which are invariably formed during the final stages of steel-making, and which would otherwise remain in the solid metal, making it hot and cold-short—*i.e.*, unworkable—and, second, to combine with the sulphur as manganese sulphide, in which state the sulphur is relatively harmless. The manganese which is in excess of these requirements has the effect of raising the hardness and tensile strength of the steel. The extent of its influence in this direction has been carefully examined by Campbell (see Chapter VII., p. 102).

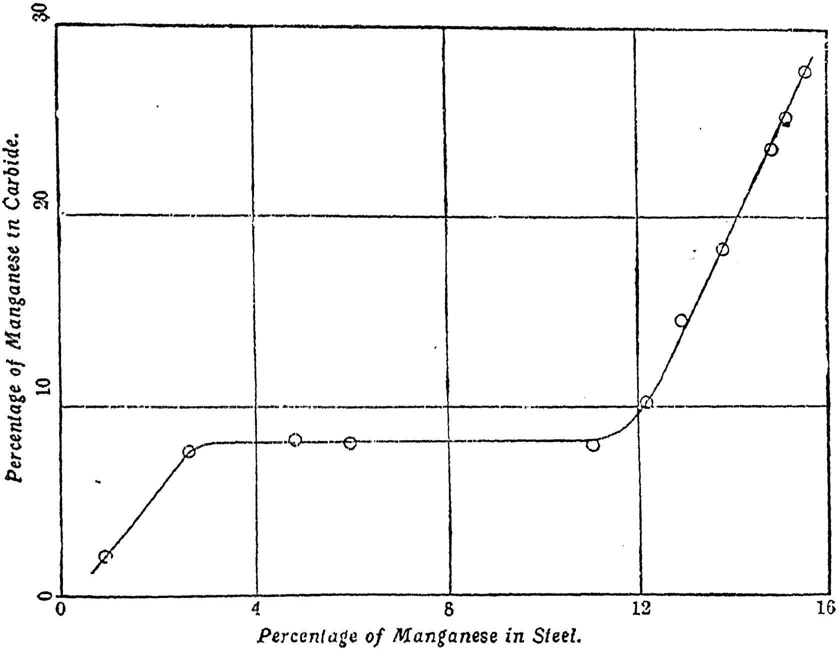


Fig. 188.

The chemical relations of iron, carbon, and manganese have been examined

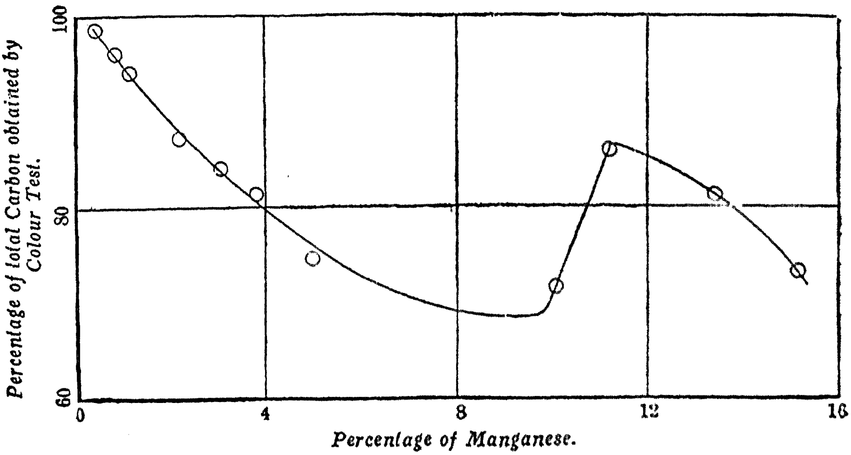


Fig. 189.

TABLE XXXVIII.

No. of Steel Ingot.	Carbon.	Manganese.	Analysis of Carbide.			Percentage of Total Carbon obtained by Carbide Residue.
			Carbon.	Iron.	Manganese.	
	Per cent.	Per cent.				
1,078	0·78	0·41	6·80	90·99	2·21	93·88
1,078	0·78	0·41	6·85	90·98	2·17	93·93
1,077	0·78	0·83	6·86	88·53	4·61	90·12
1,077	0·78	0·83	6·94	88·41	4·64	90·89
990	0·85	1·16	7·17	86·51	6·31	84·16
990	0·85	1·16	7·24	86·39	6·36	85·41
991	0·86	2·21	7·50	80·83	11·68	73·67
991	0·86	2·21	7·84	80·44	11·72	76·29
996	0·88	3·10	7·82	76·91	15·27	68·32
996	0·88	3·10	7·47	76·79	15·74	66·41
997	0·81	3·85	8·46	71·83	19·70	63·22
997	0·81	3·85	7·96	72·09	19·95	59·32
999	0·87	4·98	7·80	70·20	22·00	55·93
999	0·87	4·98	7·82	69·92	22·26	56·97
1,085	0·95	10·07	8·50	70·53	20·97	67·07
1,085	0·95	10·07	8·05	69·17	22·78	..
1,068	1·00	11·21	6·93	71·20	21·87	77·32
1,068	1·00	11·21	6·85	71·38	21·77	77·06
1,067	1·07	13·38	7·76	69·74	22·50	74·50
1,067	1·07	13·38	7·08	70·59	22·33	74·82
1,067	1·07	13·38	7·31	70·44	22·25	74·11
1,065	0·82	15·11	8·33	62·28	29·39	64·90
1,065	0·82	15·11	7·49	66·22	26·29	52·06
1,065	0·82	15·11	7·27	64·62	28·11	69·19

by Dr. Stead,[1] Professors Arnold and Read,[2] and others. By a chemical method of separation Stead obtained, from a steel containing 1·77 per cent. of carbon and 12·18 per cent. of manganese, a carbide residue which contained 17·19 per cent. of manganese. Arnold and Read's careful determinations were made with a set of twelve steels with carbon and manganese varying respectively from 0·78 to 1·07 per cent. and 0·41 to 19·59 per cent. They used an electrolytic method, which was practically the same as that by which they isolated the carbide of iron, Fe_3C from carbon steels. The figures they obtained are given in Table XXXVIII., and the manganese content of the residues are plotted as vertical ordinates, and the percentage of manganese in the steels as horizontal ordinates in fig. 188. The one striking feature about these results is that the manganese in the residues remains practically constant for steels containing from 4·98 to 13·38 per cent. of manganese. Even with these careful determinations at hand, the authors were unable to say whether the iron and manganese in the carbides are there as double compounds or simply as mixtures of iron and manganese carbides. This uncertainty is particularly evident when it is remembered that in many cases less than 70 per cent. of the total carbon contained in the steels was found in the residues. The authors say :—" It would appear

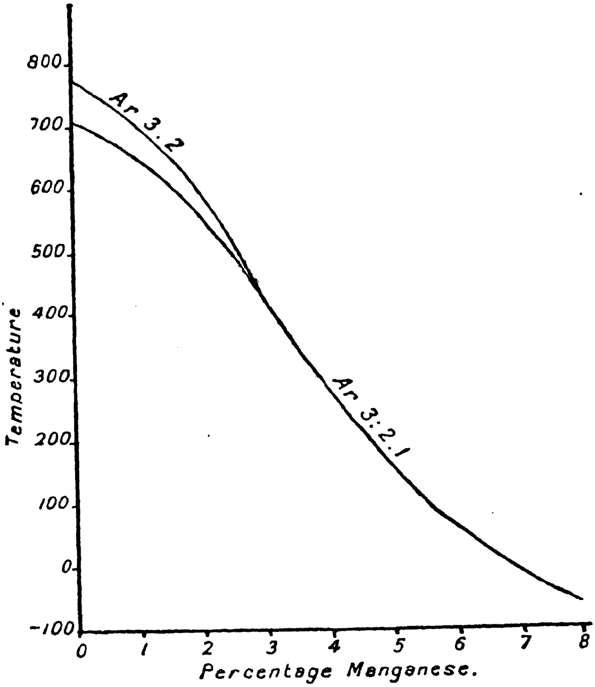


Fig. 190.

---

[1] *Journ. Iron and Steel Inst.*, 1894, No. 1, p. 192.
[2] *Journ. Iron and Steel Inst.*, 1910, No. 1, p. 169.

that the carbides from steels containing up to 4·98 per cent. of manganese are simply mixtures, and possibly a considerable amount of a true double carbide, $3Fe_3C, Mn_3C$, is present in steels containing from 4·98 to 13·38 per cent. of manganese." Another point of interest, which was first noted by Stead, is that manganese carbide gives no colouration in the carbon colour test, similar to the well-known brown colour obtained with iron carbide, when dissolved in nitric acid (specific gravity 1·20). This observation has been amply confirmed by Arnold and Read, who graphically illustrated their results as in fig. 189.

The effect of manganese upon the critical points of iron was determined by Osmond.[1] He found that these changes are almost progressively lowered with increasing percentages of manganese (see fig. 190). The magnetic change is lowered at a quicker rate than the carbide change, until with about 3·0 per cent. they are coincident at a little above 400° C. A steel with 0·45 carbon 0·11 silicon, and 4·0 per cent. of manganese has one transformation at 300° C. With 0·32 carbon, 0·26 silicon, and 5·0 of manganese the change occurs at 100° C. With from 7 to 12 per cent. or more of manganese no transformation takes place on cooling down to the ordinary temperature.

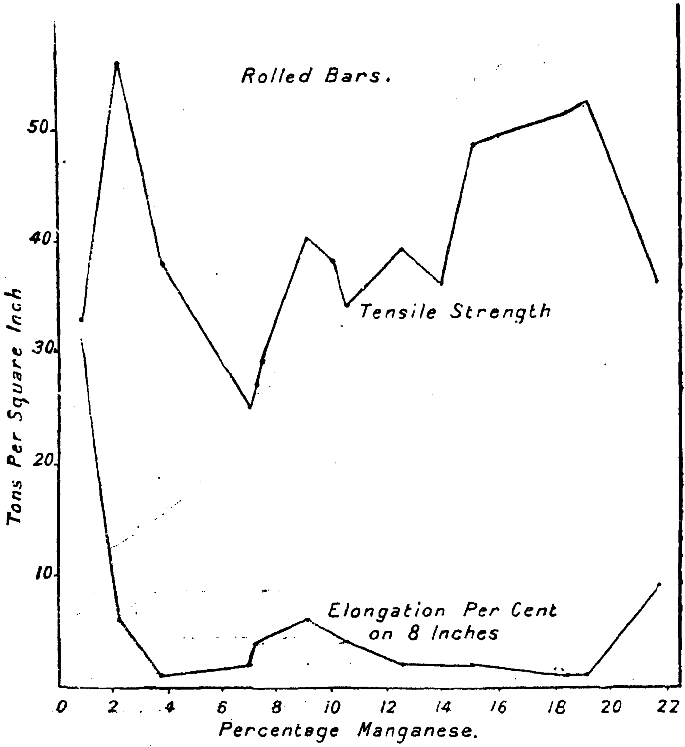


Fig. 191.

---

[1] *L'Académie des Science*, 1897.

As a result of this lowering of the thermal critical points the magnetic permeability decreases with increasing percentages of manganese, and when no transformation occurs above 0° C., as is the case when more than 7 or 8 per cent. of manganese is present, the steels are practically non-magnetic.

The only commercial manganese steel in practical use is that discovered by Sir R. Hadfield, and almost invariably described as "Hadfield's manganese steel." It usually contains from 12 to 14 per cent. of manganese, together with about 1·5 per cent. of carbon.

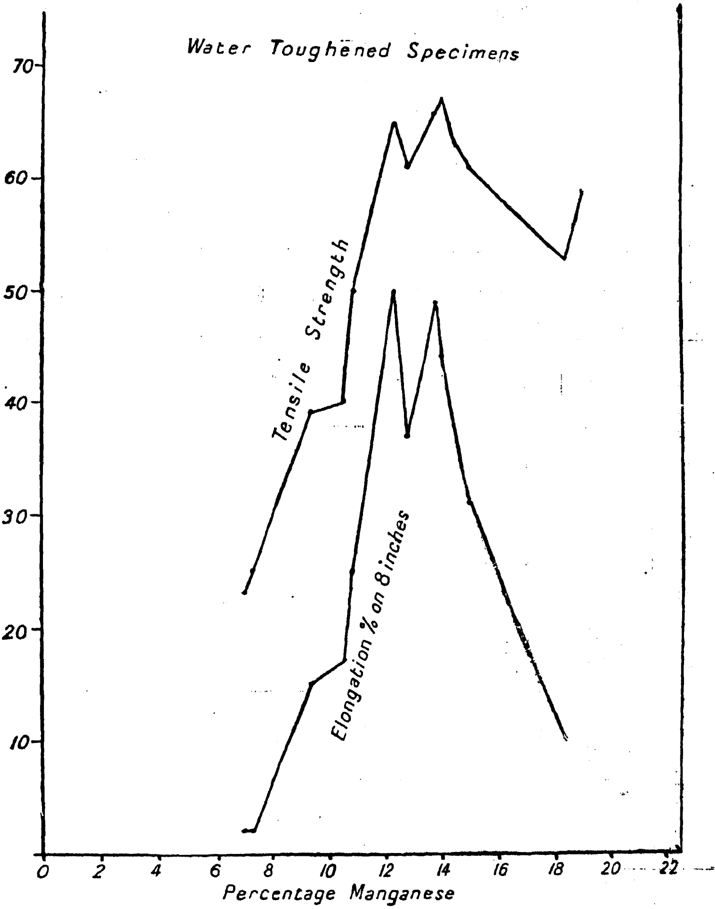


Fig. 192.

The mechanical and other properties of steels containing varying percentages of manganese have been very thoroughly investigated by its inventor,[1] and later by Dr. Guillet,[2] who has confirmed and extended these

---

[1] *Proc. Inst. of Civil Engs.*, vol. xciii.; and the *Journ. Iron and Steel Inst.*, No. 11, 1888.

[2] *Bulletin de la Société d'Encouragement pour l'Industrie Nationale*, vol. cv., pp. 421-434.

TABLE XXXIX.

Analysis per cent.			Tested in Natural Rolled State.		"Air Toughened."		"Oil Toughened."		"Water Toughened."		Remarks.
Carbon.	Silicon.	Manganese.	Tons per square inch.	Elongation per cent.	Tons per square inch.	Elongation per cent.	Tons per square inch.	Elongation per cent.	Tons per square inch.	Elongation per cent.	
0·20	0·03	0·83	33	31	..	..	..	..	..	..	Reduction in area, 46 per cent
0·40	0·15	2·30	56	6	..	..	..	..	..	..	Reduction in area, 7 per cent.
0·40	0·09	3·89	38	1	..	..	..	..	..	..	
0·52	0·37	6·95	25	2	21	2	19	2	23	2	
0·47	0·44	7·22	27	2	27	5	25	3	25	2	
..	..	7·50	39	4	..	..	..	..	..	..	Reduction in area, 9 per cent.
0·50	0·28	7·90	..	..	28	8	30	7	..	..	
1·00	0·42	9·15	..	..		..	42	17	..	..	
..	..	9·20	40	6	..	..	..	..	..	..	Reduction in area, 10 per cent.
0·61	0·30	9·37	33	5	38	16	38	15	39	15	
0·95	0·21	10·11	38	5	39	14	41	20	..	..	
0·85	0·28	10·60	34	4	41	17	42	19	40	17	
0·72	0·37	10·83	..	..	..	..	..	..	50	25	
									63	45	
0·85	0·37	12·29	.	..	..	..	..	..	64	45	
									65	50	
1·10	0·16	12·6	39	2	37	11	50	28	54	27	
0·92	0·42	12·8	39	5	48	20	58	32	61	37	
0·85	0·23	13·75	..	..	..	..	..	..	66	49	Still unbroken.
0·85	0·28	14·01	36	2	48	14	55	27	67	44	
1·15	0·84	14·27	..	..	..	..	..	..	69	46	Reduction in area, 37 per cent.
1·10	0·32	14·48	39	1	49	5	..	..	63	37	
1·24	0·16	15·06	49	2	47	2	..	..	61	31	
1·54	0·16	18·40	51	1	39	1	..	..	53	10	
1·83	0·26	18·55	43	1	..	..	..	..	55	5	
1·60	0·26	19·1	52	1	41	1	..	..	59	4	
1·90	0·32	19·98	..	..	..	..	23	nil	..	..	
2·10	0·46	21·69	36	9	34	12	33	11	..	..	

observations. Some of the results obtained by Hadfield are given in Table XXXIX., and plotted in figs. 191 and 192.

Considering the steels in their normal rolled condition, it will be noticed that the first effect of manganese is considerably to raise the tensile strength and lower the elongation, with 2·3 per cent. of manganese the figures are respectively 56 tons per square inch and 6·0 per cent. on 8 inches. With from 3·89 to 7·22 per cent. of manganese they are exceedingly brittle, as is indicated by the low ultimate stress and inappreciable elongation. There is a marked improvement in the tensile properties as the manganese content is raised from 7·5 to 12·7 per cent., but with further increase the elongation is generally below 2·0 per cent.; the only exception being the steel with 21·69 per cent. of manganese, which gave an elongation of 9·0 per cent. Some of the irregularities in the mechanical properties of these steels are to some extent accounted for by the variations in the percentages of carbon.

The most remarkable property of these steels, which was discovered by Hadfield, is their power of being toughened by a treatment which would cause brittleness, water cracking, and other defects in carbon steels. This process of "water toughening" consists in heating to a high temperature 1,000° to 1,100° C., followed by relatively quick cooling in air, oil, or water. It can be applied with equally good results to material in its cast or rolled condition. The advantages obtained are most noticeable when the manganese content is between 10 and 14 per cent. Thus, for example, by heating and then quenching in water the tensile strength can be raised to 65 tons per square inch, whilst the elongation is also raised from about 6·0 to 6·5 per cent. on 8 inches. It is a very remarkable fact that this increased ductility, or what may be regarded as greater softness, renders the steel but little easier to file.

Speaking of the peculiar kind of hardness of manganese steels, Sir Robert Hadfield says:—"It is difficult accurately to describe this quality, because all the specimens are exceedingly hard in their cast and forged condition; in fact, it is scarcely possible to machine any of them on a practical scale, yet such hardness varies considerably in degree, being most intense in the cast material containing 5 to 6 per cent. of manganese, which no tool will face or touch. A gradual decrease then occurs, and when about 10 per cent. is reached the softest condition occurs. Then an increase again takes place, and at 22 per cent. it is very hard, still not so much so as the 5 per cent. Although the 8 to 20 per cent. steels can be machined, it is only with the utmost difficulty, as will be seen from the following example:—The test bar (No. 22 B.), containing 14 per cent. of manganese, which gave an elongation of 44·5 per cent. without fracture, and had a tensile strength of 67 tons, was put under a double-geared 18-inch drill. Over an hour was occupied in drilling one hole ½ inch in diameter by ¾ inch deep, and even to do this it was requisite to run at the lowest speed, or the edge of the drill would have given way. . . . Yet this specimen could be indented by an ordinary hand hammer, so that whilst so hard it may be said to possess 'a special kind of softness.' Although when being turned it appears harder than chilled iron, its softness is particularly noticeable when testing the material for compression."

CHAPTER XX.

CHROMIUM.

CHROMIUM is employed as a special addition to steels which consist almost exclusively of iron-carbon and chromium, but it is even more widely used in conjunction with other elements, such as nickel or tungsten, etc., in quaternary steels.

A study of its influence in the ternary steels is necessary, not only to understand how such steels should be treated, but in order to determine its function in the more complicated quaternary mixtures as well. There can be no doubt that the action of this element, whether in ternary or quaternary mixtures, is, broadly speaking, that of a hardener. It is, therefore, used either to raise the tensile strength of steel for certain special mechanical purposes, or to increase the abrasive hardness, as in the case of tool steels, or the resistance to penetration, as in the case of armour plates, etc.

Osmond[1] considered that chromium might exist in three conditions, which might or might not exist together according to the composition of steel. These are as follows :—

1st. In the state of dissolved chromium (in the iron).

2nd. As a compound of chromium, iron, and carbon, which exists in the form of isolated globules.

3rd. The above compound may exist in the form of a solid solution in the iron.

By a chemical means of separation Carnot and Gontal[2] obtained a residue corresponding to the formula Fe_3C, $3Cr_3C$ from a ferro-chromium, and $3Fe_3C + Cr_3C_2$ from two chromium steels.

TABLE XL.

Analysis.		Percentage of Total Carbon obtained in Carbide Residue.	Analysis of Carbide.			Corresponding to Formula.
Carbon.	Chromium.		Carbon.	Chromium.	Iron.	
0·64	0·65	94·28	6·95	4·12	88·93	$20Fe_3C$, Cr_3C_2.
0·64	0·65	99·37	7·08	4·56	88·35	
0·64	0·65	98·84	7·12	4·41	88·47	
0·84	0·99	85·72	7·20	6·99	85·80	$12Fe_3C$, Cr_3C_2.
0·84	0·99	82·17	7·27	7·22	85·51	
0·835	4·97	85·54	9·04	45·67	45·29	$4Fe_3C$, $3Cr_3C_2$, Cr_4C.
0·835	4·97	80·73	8·69	45·81	45·52	
0·85	10·15	87·05	8·16	63·51	28·38	Fe_3C, Cr_3C_2, Cr_4C.
0·85	10·15	84·77	8·23	62·83	28·93	
0·88	15·02	97·41	6·05	59·34	34·60	$2Fe_3C$, $3Cr_4C$.
0·88	15·02	99·70	5·96	59·49	34·54	
0·85	19·46	..	5·58	60·93	33·49	
0·85	19·46	99·19	5·21	62·13	32·66	
0·85	23·70	..	5·05	62·83	32·12	

---

[1] Report on Sir Robert Hadfield's paper, *Iron and Steel Inst.*, No. 2, 1892.

[2] *Comptes Rendus*, 1898, vol. cxxvi., p. 1243.

Professors Arnold and Read[1] have conducted a series of experiments in order to determine the chemical constitution of annealed chromium steels. The steels they examined contained from 0·64 to 0·85 per cent. of carbon and 0·65 to 23·7 per cent. of chromium. The results they obtained are given in Table XL., and the percentages of chromium and carbon co tained in the carbide residues obtained from the various steels are plott graphically in figs. 193 and 194.

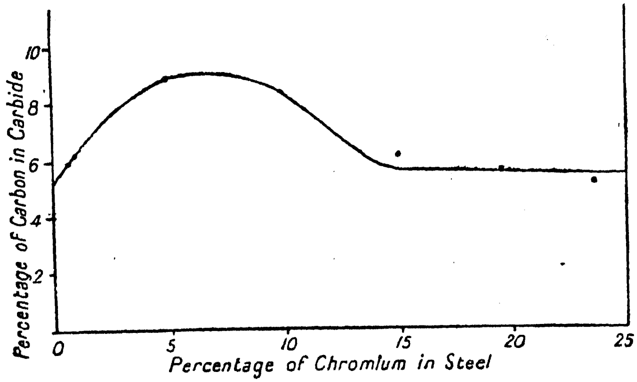


Fig. 193

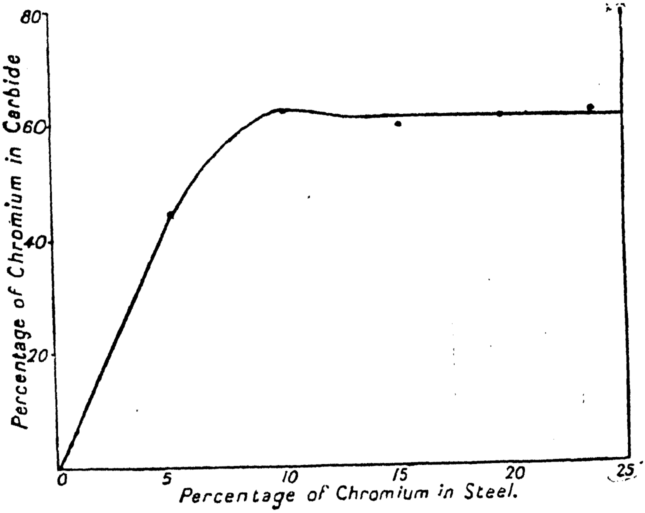


Fig. 194.

The effect of chromium upon the temperature at which the normal critic points of iron and carbon steel occur was very carefully investigated l

---

[1] *Journ. Iron and Steel Inst.*, No. 1, 1911, p. 249.

TABLE XLI.

No.	Analysis.				Ar$_3$.			Ar$_2$.			Ar$_1$.		
	Carbon.	Silicon.	Man-ganese.	Chromium	Beginning	Maximum between	End about	Beginning about	Maximum between	End about	Beginning about	Maximum between	End about
1	0·16	0·07	0·18	0·29	865° C.	845–835°	825°	755°	740–730°	720°	680°	680–670°	660°
2	0·15	0·10	0·21	0·48	835° C.	810–800°	785°	740°	720–710°	700°	690°	680–670°	660°
3	0·12	0·08	0·18	0·84	825° C.	805–795°	785°	740°	720–710°	700°	700°	690–680°	670°
4	0·27	0·12	0·21	1·18	. .	. .	. .	780°	760–750°	725°	700°	700–690°	680°
5	0·77	0·50	0·61	5·19	. .	. .	. .	780°	740°	720°	recalescence at 682–692° C.		
6	0·71	0·36	0·25	9·18	. .	. .	. .	. .	. .	. .	recalescence at 684–704° C.		

Osmond, who worked with Sir Robert Hadfield's steels, and published the results in a report on the latter's paper. These results are extremely interesting, and should be carefully studied, because they show that chromium occupies what may be regarded as a unique position in the metallurgy of steel. The position of the critical points on cooling from 1,030° C. are given in Table XLI. It will be noticed that there is a tendency for the temperature at which the Ar_1 change takes place to be raised as the percentage chromium is increased.

Working with other steels, and considering the Ar_1 point, Professor Carpenter[1] says:—" Increase of chromium tends to raise the critical point. Thus, comparing the values obtained on cooling from about 900° C.:—

" STEELS USED BY PROFESSOR CARPENTER.

Composition.		
Carbon.	Chromium.	Ar_1 Change.
0·29	3·24	738° C.
0·54	1·12	729° C.
1·09	9·55	776° C."

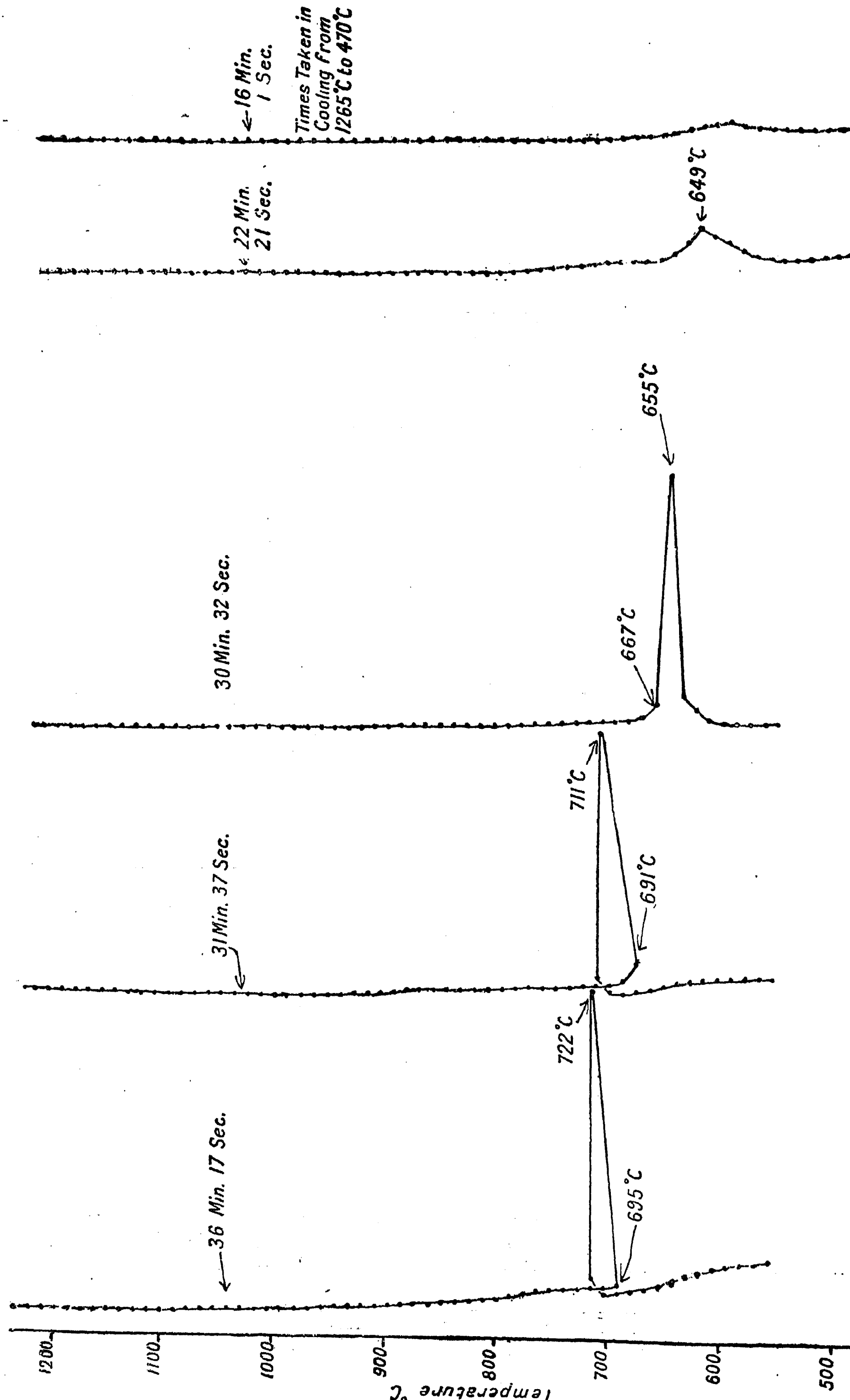
He regarded the raising of this critical point " as due either to chromium or chromium jointly with carbon." From other considerations the present author[2] concluded that the latter is the correct view. All the above results refer to the temperature of the change when the steel is cooled slowly, and, considered alone, they certainly indicate that chromium facilitates the change. There is, however, another view to take—namely, variations in the rate of cooling. It was shown in Sir R. Hadfield's work that some of the steels experimented with are extraordinarily sensitive to moderately quick cooling in air. This is especially so for steel No. 5, Table XLI., which, as Osmond said, " is as well hardened by simply cooling in air as ordinary carbon steels by quenching in water." This was explained by the fact that, although the cooling velocity is not so great, the presence of the chromium acts in the same way in suppressing the change.

Kikkawa and the author have obtained definite evidence in this connection by taking cooling curves (fig. 195) from a constant temperature at known varying rates of cooling over a determined range of temperature. These curves very clearly illustrate what may be justly termed " the critical cooling velocities " for a steel containing 6·15 per cent. of chromium and 0·63 per cent. of carbon, for they show that if the cooling from 1,230° C. to 550° C. takes place in 16 minutes the carbide change is suppressed, and the steel is as hard as water-quenched carbon steel, whereas if the cooling over the same range of temperature takes 30 minutes, the material is practical in the soft annealed state as a result of the change having occurred. In addition to this remarkable effect which is produced by such comparatively insignificant variations in cooling, it should be noted that the effect of initial temperature is equally important. Whilst this has not yet been so thoroughly elucidated, Kikkawa and the author have obtained some instructive results, which are given in Table XLII., and plotted

---

[1] *Journ. Iron and Steel Inst.*, No. 1, 1905, p. 433.

[2] *Journ. Iron and Steel Inst.*, No. 2, 1908, p. 104.


Times Taken in Cooling from 1265°C to 470°C
16 Min. 1 Sec.
22 Min. 21 Sec.
649°C
30 Min. 32 Sec.
655°C
667°C
31 Min. 37 Sec.
711°C
691°C
36 Min. 17 Sec.
722°C
695°C
1200
1100
1000
900
800
700
600
500
Temperature °C

in fig. 199. These show the Brinell hardness numbers of the same chromium steel after heating cubic-inch specimens in a furnace to the temperatures mentioned, and then taking them out of the furnace and allowing them to cool on an asbestos pad in air.

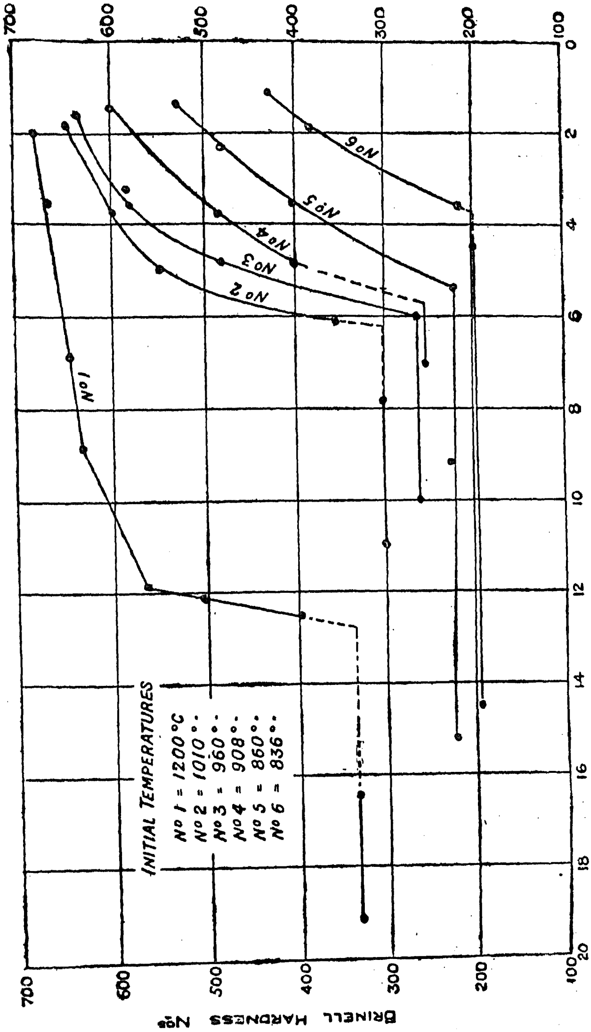


Fig. 196.— Effect of Initial Temperature on Critical Cooling Velocities and Hardness.

Another method of illustrating the influence of initial temperature is depicted in fig. 196. In this case the samples were heated to the six recorded temperatures maintained at those temperatures for half-an-hour, and then cooled at certain known rates. The rates of cooling, which are plotted, correspond to the times taken in cooling over the same range of temperature in each case—namely, from 836° C., which is 25° C. above the thermal change on heating, to 546°, which is well below the normal temperature of the corresponding change on cooling. After each experiment the Brinell hardness was determined, and these have been plotted against the cooling rates. The chief characteristics of the cooling curve obtained are the same as those shown in fig. 195. The horizontal branch of the hardness curves correspond with the cooling rates which permitted the whole of the carbide transformation to take place at approximately the normal temperature, and the sudden rise in hardness with the beginning of the suppression of that change. It will be noticed that even though the whole of the carbide change occurs with comparatively slow rates of cooling from each initial temperature, the hardness of the steel increases quite considerably with the initial temperature from which it was cooled. Further, with any given rate of cooling the hardness of the metal increases with the temperature to which it was heated. These results very clearly demonstrate that both the degree of hardness attained and the facility with which a steel of this kind is hardened becomes greater as the initial temperature is raised. The precise cause of the difference which is produced in this way is not known with any certainty. The view which was provisionally advanced by Messrs. Kikkawa, Greenwood, and the author[1] was that the chromium carbide $(Cr_3C_2)_n$ first goes into solution as $(Cr_3C_2)_2$, and is then progressively dissociated into Cr_3C_2 as the temperature is raised. When the steel is again being cooled these molecules only slowly re-associate, and thus the molecular effect of the dissolved chromium carbide is greater as the initial temperature and molecular dissociation increases. This increased number of molecules in solution then enables the carbide point to be more readily suppressed. In a remarkably

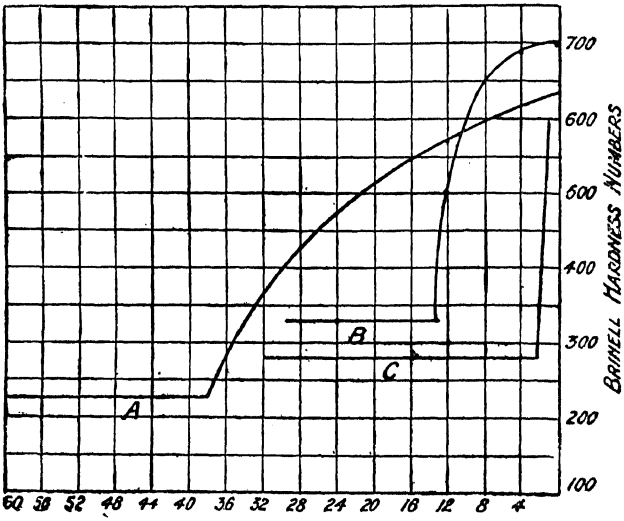


Fig. 197.—Cooling Rate in Minutes.

---

[1] *Journn. Iron and Steel Inst.*, 1916, No. 1.

good investigation on the magnetic transformation points of chromium-carbon steels, Takejiro Murakami[1] considers that dissociation of the carbides in solution occurs when the temperature is progressively raised above the Ac_1 point, but he is of the opinion that the reaction which occurs is expressed by the equation—

$$2Cr_4C = Cr_3C_2 + 5Cr.$$

The above-mentioned critical cooling rates are, as would be anticipated, very materially influenced by the carbon and chromium contents of the steel. The influence of carbon in this connection is clearly indicated in fig. 197, in which are represented the hardnesses, plotted against cooling rates, of three steels containing different percentages of carbon, but practically the same amounts of chromium. The compositions of the three specimens were—

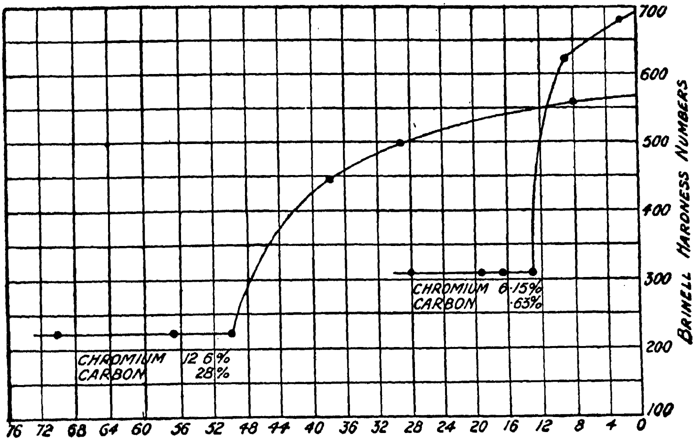


Fig. 198.—Cooling Rate in Minutes.

TABLE XLII.

Temperatures from which the Specimens were cooled in Air.	Brinell Hardness Numbers.
800° C.	288·3
870° C.	313·6
930° C.	494·3
955° C.	606·3
1,025° C.	646·9
1,060° C.	641·7

A, . . .	6·18 per cent. chromium.	0·37 per cent. carbon.
B, . . .	6·15 „ „	0·63 „ „
C, . . .	6·16 „ „	0·97 „ „

The data for the steel containing 12·6 per cent. of chromium and 0·28 per cent. of carbon are plotted in fig. 198.

---

[1] *Science Reports of the Tôhoku Imperial University*, vol. vii., No. 3. p. 217.

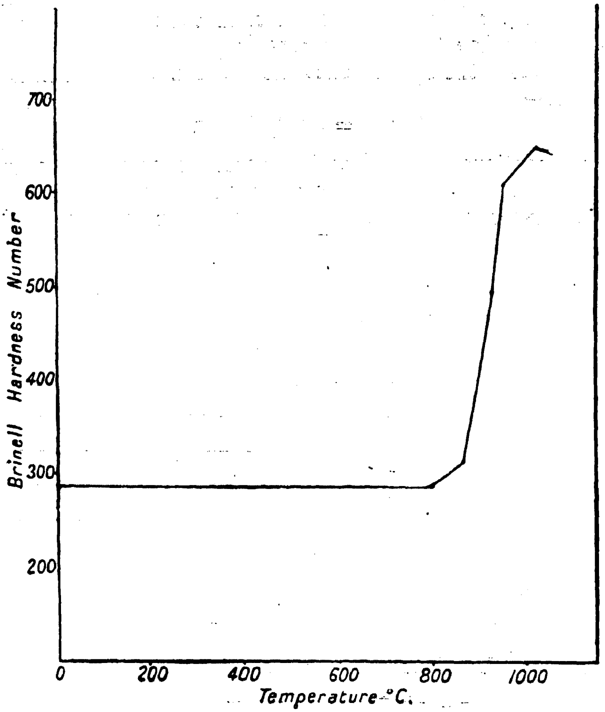


Fig. 199.

TABLE XLIII.—Composition of Hadfield's Chromium Steels.

No.	Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Chromium.
1	0·07	0·07	0·09	0·04	0·11	0·22
2	0·16	0·07	0·10	0·04	0·18	0·29
3	0·15	0·10	0·09	0·04	0·21	0·48
4	0·14	0·08	0·09	0·04	0·25	0·57
5	0·12	0·08	0·10	0·04	0·18	0·84
6	0·27	0·12	0·13	0·04	0·21	1·18
7	0·21	0·14	0·09	0·04	0·12	1·51
8	0·39	0·14	0·11	0·04	0·25	2·54
9	0·41	0·18	0·10	0·04	0·28	3·17
10	0·77	0·50	0·11	0·04	0·61	5·19
11	0·86	0·31	0·13	0·03	0·29	6·89
12	0·71	0·36	0·10	0·03	0·25	9·18
13	1·27	0·38	0·10	0·03	0·25	11·13
14	1·79	0·61	0·08	0·04	0·28	15·12
15	2·12	1·20	0·10	0·04	0·22	16·74

The mechanical properties of chromium steels have formed the subject of an important paper by Sir Robert Hadfield already referred to. Some of the more important data contained therein are embodied in Tables XLIII., XLIV., and XLV. From these figures it will be seen that increasing percentages of chromium bring about a substantial increase in the tensile strength of the steels, with a corresponding diminution in the ductility. This is the case until about 5·19 per cent, is present, after which further additions appear to soften the metal—*i.e.*, increase the ductility and lower

TABLE XLIV.—MECHANICAL PPOPERTIES OF ROLLED BARS (UNANNEALED).

No.	Elasti Limit.	Ultimate Stress.	Elongation.	Reduction of Area.
	Tons per sq. inch.	Tons per sq. inch.	Per cent.	Per cent
1	19·50	28·00	38·65	64·12
2	21·00	28·00	41·95	67·06
3	22·50	31·00	37·75	43·92
4	21·00	29·00	41·00	68·48
5	22·00	31·50	40·00	62·14
6	26·00	39·50	33·80	56·22
7	24·00	38·00	37·10	64·12
8	29·50	54·00	26·75	51·98
9	30·00	64·00	21·65	43·84
10	40·00	74·00	13·05	20·16
11	40·00	72·50	13·55	26·74
12	30·00	61·00	17·65	27·58
13	30·00	2·00	10·38	11·66
14	..	..	..	..
15	..	..	..	..

TABLE XLV.—MECHANICAL PROPERTIES OF ANNEALED BARS.

No.	Elastic Limit.	Ultimate Stress.	Elongation.	Reduction of Area.
	Tons per sq. inch.	Tons per sq. inch.	Per cent.	Per cent.
1	16·50	24·00	45·20	68·20
2	17·00	25·00	45·55	65·90
3	18·00	27·50	44·90	61·98
4	15·00	25·50	46·60	69·04
5	19·00	28·00	42·50	61·20
6	20·00	36·00	32·95	46·80
7	19·00	33·50	38·07	55·88
8	24·50	44·00	22·50	33·84
9	21·50	47·50	24·05	35·46
10	20·00	55·00	8·20	6·88
11	19·00	41·00	34·75	45·52
12	18·00	44·00	25·00	32·82
13	..	33·00	..	..
14	19·50	44·00	9·55	7·84
15	..	..	..	..

the tensile strength. This softening is quite marked, when it is remembered that in the steels mentioned the percentage of carbon was somewhat irregular, and with one exception was higher as the percentage of chromium was raised above 5·19.

Perhaps a better idea of the effect of chromium can be gained on examining figs. 200, 201, and 202, taken from Dr. Guillet's work,[1] in which are illustrated the hardness and tensile properties of two series of steels containing respectively 0·20 and 0·80 per cent. of carbon with varying percentages of chromium. It will be noticed that in the series with 0·20 per cent. of carbon the maximum hardness is reached with about 10·0 per cent. of chromium, whilst with 0·80 per cent. of carbon the corresponding maximum occurs at 14·5 per cent. of chromium. With the 0·20 per cent. carbon series the highest tensile strength is obtained with 7·5 of chromium, but at 2·0 per cent. of chromium with 0·80 of carbon. From what has been said in regard to the effect of slight variations in the rate of cooling upon the carbide change in chromium steels, and also of initial temperature upon the hardness of air-cooled specimens, it is clear that these steels are extremely sensitive to heat treatment. In fact, the element chromium imparts to steel a much greater degree of the property known as "air hardening" than the element tungsten. On the other hand, air-hardened chromium steels lose their hardness at a low temperature, but this tempering of the steel is rendered more difficult by the addition of tungsten.

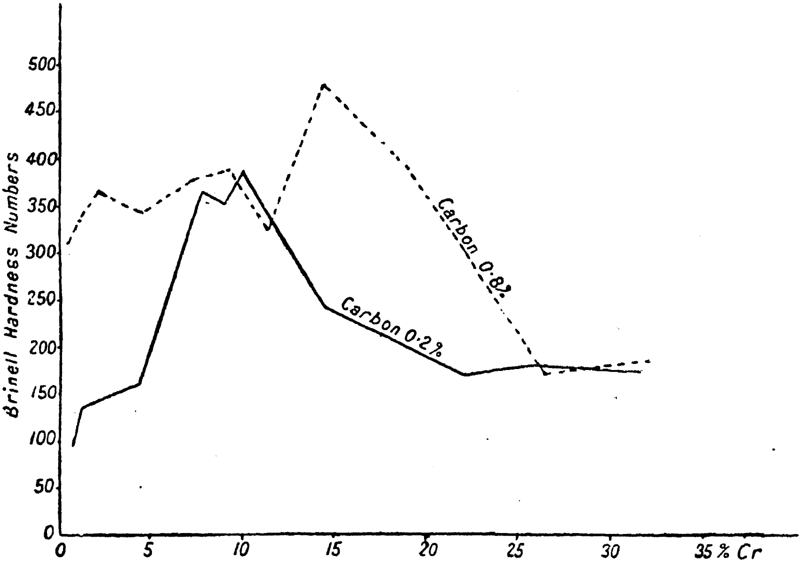


Fig. 200.

---

[1] *Revue de Metallurgie,* 1904, pp. 155-183.

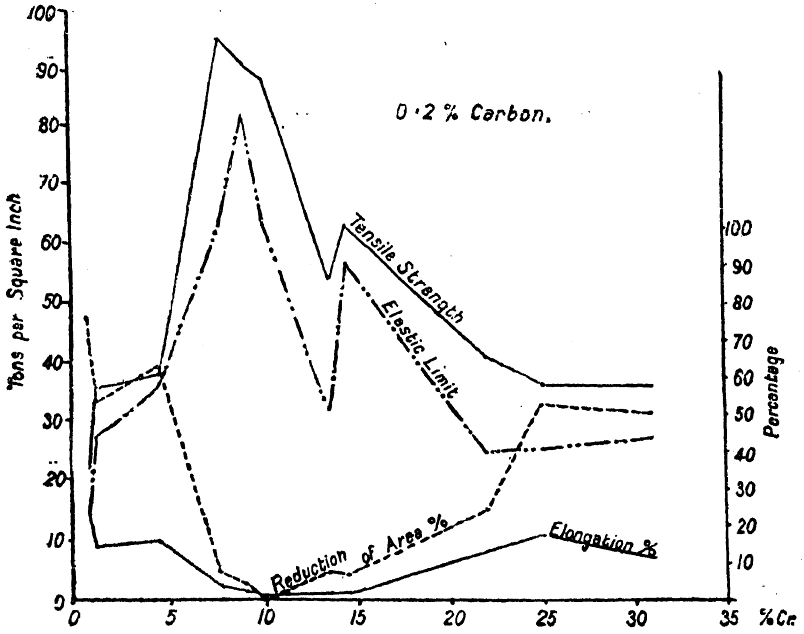


Fig. 201.

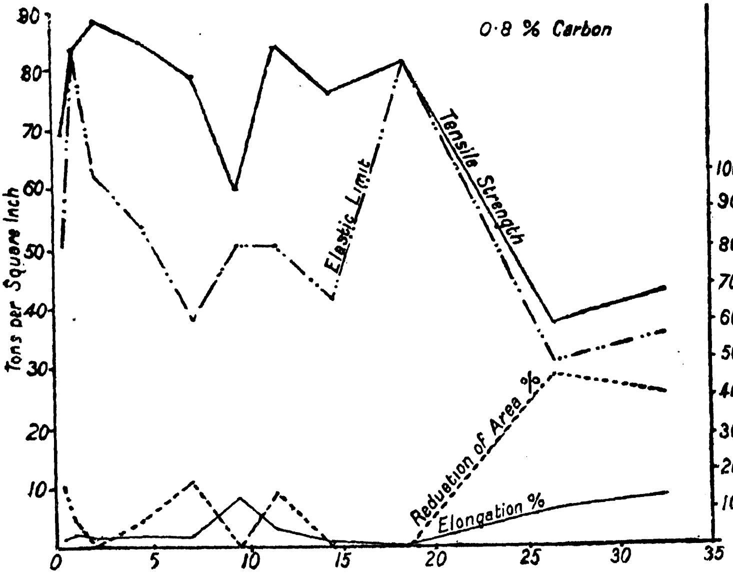


Fig 202.

CHAPTER XXI.

ALUMINIUM, SILICON, AND VANADIUM.

THE effect of aluminium and silicon upon steel may conveniently be considered together, since their action is in many respects very similar. In small quantities they are both very widely used in steel metallurgy for the purpose of improving the casting qualities of the metal, and in the manufacture of what is known as "ingot iron," which is practically pure iron made in basic open-hearth steel furnaces, even traces of aluminium have a very pronounced influence in this respect, and also make the material much more suitable for rolling purposes. This is brought about by the reduction of the oxide of iron, which may be dissolved in the liquid metal, and also, as Brinell has shown (see Chapter VI.), by increasing the solubility of gases such as nitrogen and carbon-monoxide in the solid metal. This increased solubility delays the separation of the gases from the mass during its solidification, and thus hinders the formation of blowholes in the ingot.

By carefully controlling the percentage of aluminium and silicon in ingot iron, or steel, blowholes can be completely prevented. If, however, too much aluminium or silicon be used, the metal will be what is technically known as "killed," and will undergo relatively considerable contraction during solidification, with the result that large deep-seated pipe cavities are formed in the ingot.

Steels containing about 0·75 per cent. of aluminium or silicon are very difficult to cast; they are viscid and sluggish. This is due to the presence of the oxides of alumina or silicon on the surface of the liquid metal, which are very tenacious, and form on all freshly exposed surfaces. Owing to the same cause, the introduction of aluminium to almost all other metallic alloys gives the same trouble, and makes it a difficult matter to produce sound castings unless special precautions be taken. In the case of aluminium bronzes, it has been shown by Professor Carpenter and the author[1] that this troublesome feature can be entirely overcome by pouring the metal into the mould in such a way that the surface of the liquid after entering the mould is not disturbed to an appreciable extent.

So far as is known, neither aluminium nor silicon in steel have any effect upon the chemical relations of carbon and iron. In other words, the carbon in such steel when in the annealed condition is present as the carbide Fe_3C.

The most important publications relating to the mechanical properties of aluminium steels are those of Sir Robert Hadfield[2] and Dr. Guillet,[3] and for silicon steels Sir Robert Hadfield,[4] Dr. Guillet,[5] Professor Turner,[6] and Mr. T. Baker.[7]

---

[1] *Inst. Mech. Engs.*, 1910.

[2] *Journ. Iron and Steel Inst.*, 1890, No. 2.

[3] *Revue de Metallurgie*, 1905, pp. 312-327.

[4] *Journ. Iron and Steel Inst.*, 1889, No. 2, p. 222.

[5] *Revue de Metallurgie*, 1904, pp. 46-67.

[6] British Association Meeting, 1888.

[7] *Journ. Inst. of Elec. Engs.*, vol. xxxiv., p. 498, 1905.

As regards the influence of aluminium, it has been shown that, with steels containing about 0·2 per cent. of carbon, as much as 5·0 per cent. of aluminium can be present without producing any appreciable change in the tensile properties of the steels. With 7·0 per cent. the metal becomes very brittle (see fig. 203). Shock tests, however, reveal that, although small percentages of aluminium have no influence, great brittleness is evident with 2·0 per cent. Aluminium does not appear to have any effect upon the

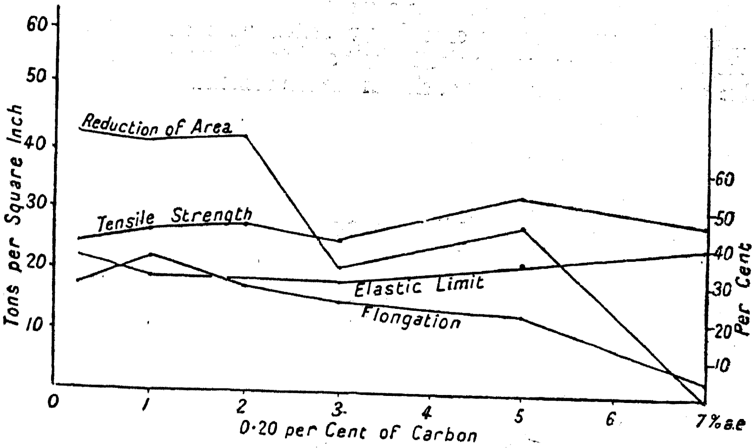


Fig. 203.

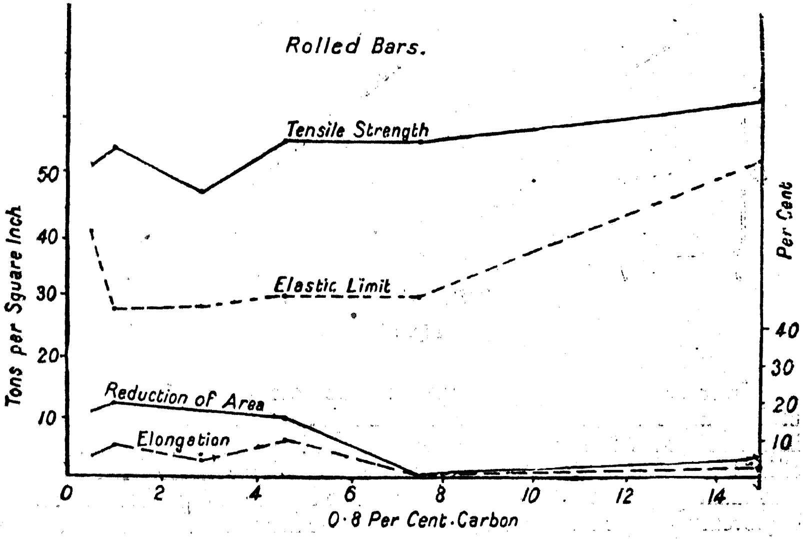


Fig. 204.

mechanical properties of steel containing about 0·75 per cent. of carbon (fig. 204). This applies both to tensile and shock tests.

The mechanical properties of silicon steels, as determined by Dr. Guillet, are given in figs. 205 and 206. The chief feature to note is that the 0·20 per cent. carbon series becomes exceedingly brittle with about 5·0 per cent. of silicon. In both series the elastic limit and tensile strength are somewhat higher than pure carbon steels of similar carbon content.

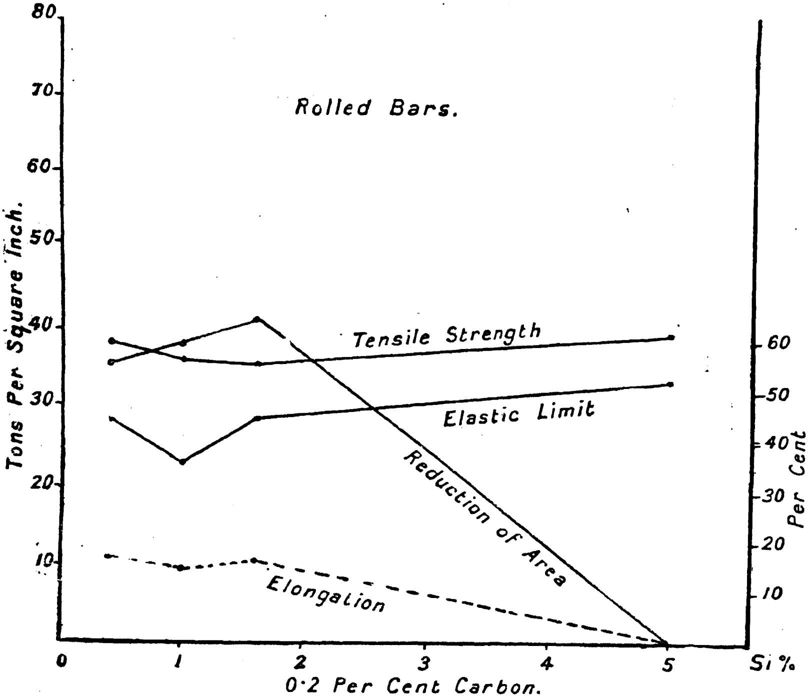


Fig. 205.

Vanadium Steels.—In view of the fact that vanadium is now used in a great many special steels, and particularly in those employed in the motor-car industry, and also high-speed cutting tools, a knowledge of its action upon carbon steels is a matter of first importance. It is claimed that small quantities of this element added to liquid steel produce a marked improvement in the mechanical properties of the metal, and certainly increase the cutting efficiency of tool steel. These improvements have been observed even when the presence of the element cannot be detected in the finished material. In such cases it is generally considered that it acts as a cleanser by removing or neutralising the gaseous impurities contained in the liquid. Quite apart from its action in this respect, low percentages of vanadium are decidedly advantageous, and it is only the high cost which prevents it being more extensively used.

As regards the chemical constitution of vanadium steels, W. Giesen[1] states that with low percentages the vanadium is completely held in solid solution by ferrite, which will dissolve up to 0·6 per cent. of vanadium. Nicolardot[2] obtained a residue from a steel containing 0·4 per cent. of carbon and 1·5 per cent. of vanadium, which corresponded in composition to the formula Fe_3C, $38(V_3C_2)$, and Fe_3C, $60(V_3C_3)$ from a steel with 0·80 per cent. of carbon and 10 per cent. of vanadium. Putz[3] found that steels containing 1·64 of vanadium and 2·0 of carbon contained the vanadium as V_2C_3.

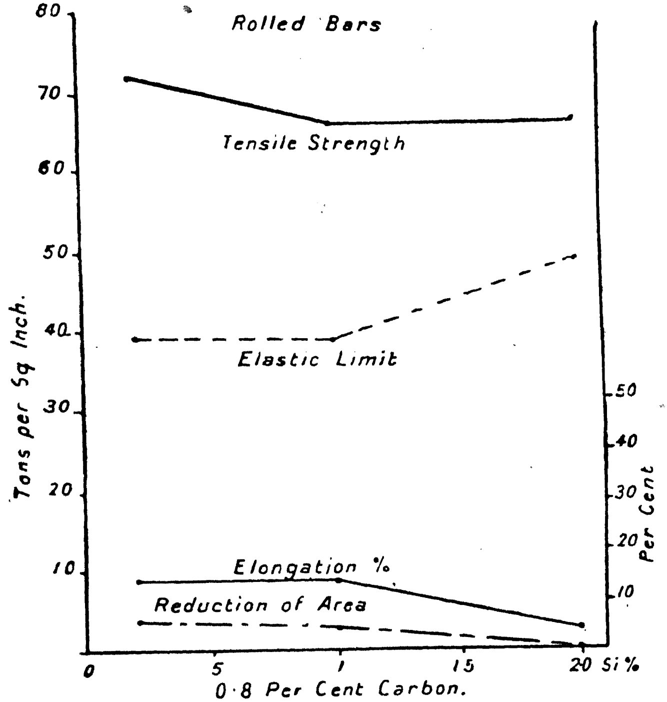


Fig. 206.

Very complete and systematic determinations relating to the chemical constitution of vanadium-carbon steels have been made by Professors Arnold and Read.[4] Their investigations were made with steels containing from 0·60 to 1·10 per cent. of carbon and from 0·71 to 13·45 per cent. of vanadium. The data they obtained are given in Table XLVI., and the more important details are plotted in figs. 207 and 208. These results clearly indicate that, as the vanadium in the steels increases, the amount of iron found in the carbide residue falls and the percentage vanadium in the same increases.

[1] *Journ. Iron and Steel Inst.*, 1909, Carnegie Memoir, vol. i.
[2] *Le Vanadium*, 1905, p. 147.
[3] *Metallurgie*, 1906, p. 651.
[4] *Journ. Iron and Steel Inst.*, 1912, No. 1, p. 215.

This displacement of the iron by vanadium is practically complete in steels containing more than 5 81 per cent. of the latter element and less than 1·10 per cent. of carbon. The carbon then exists as carbide of vanadium, V_4C_3.

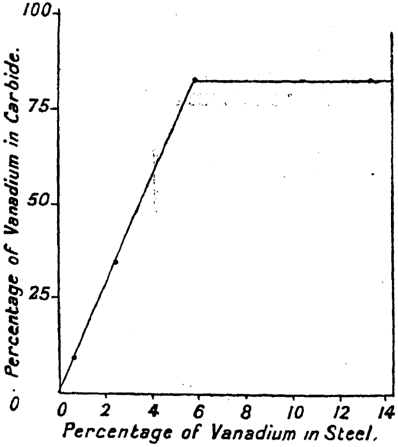


Fig. 207.

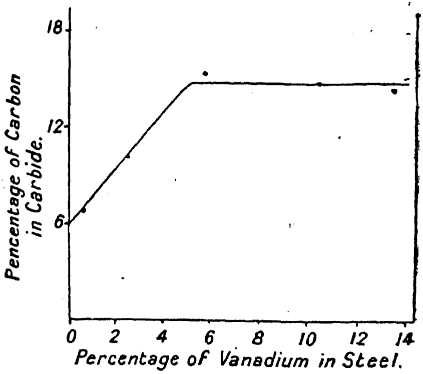


Fig. 208

The authors mentioned in their paper that "the steels dissolved quite readily, and with each member of the series vanadium was found in the hydrochloric, acid solutions"; this fact supports Giessen's statement that ferrite dissolves vanadium.

TABLE XLVI.

Analysis.		Percentage of Total Carbon obtained in Carbide Residue.	Analysis of Carbide.			Corresponding to the Formula.
Carbon.	Vanadium.		Carbon.	Iron.	Vanadium.	
0·60	0·71	95·77	7·61	83·71	8·68	$11Fe_3C + V_4C_3$.
0·60	0·71	96·98	7·66	83·69	8·65	
0·60	0·71	92·71	7·49	83·27	9·24	
0·63	2·32	88·10	10·66	54·60	34·74	$2Fe_3C + V_4C_3$.
0·63	2·32	82·80	10·44	54·71	34·85	
0·63	2·32	91·20	10·63	53·30	36·07	
0·93	5·84	99·15	15·94	0·54	83·52	V_4C_3.
0·93	5·84	98·19	15·94	0·47	83·59	
0·93	5·84	97·63	16·05	0·83	83·12	
1·07	10·30	96·76	15·03	1·04	83·93	
1·07	10·30	95·22	15·00	0·63	84·37	
1·10	13·45	99·78	14·12	0·82	85·06	
1·10	13·45	99·06	13·76	1·27	84·97	

Professors Arnold and Read also made some very interesting observations in regard to the effect of vanadium upon the critical points of iron. Thus, they found that a steel containing 0·63 per cent. of carbon and 2·32 per

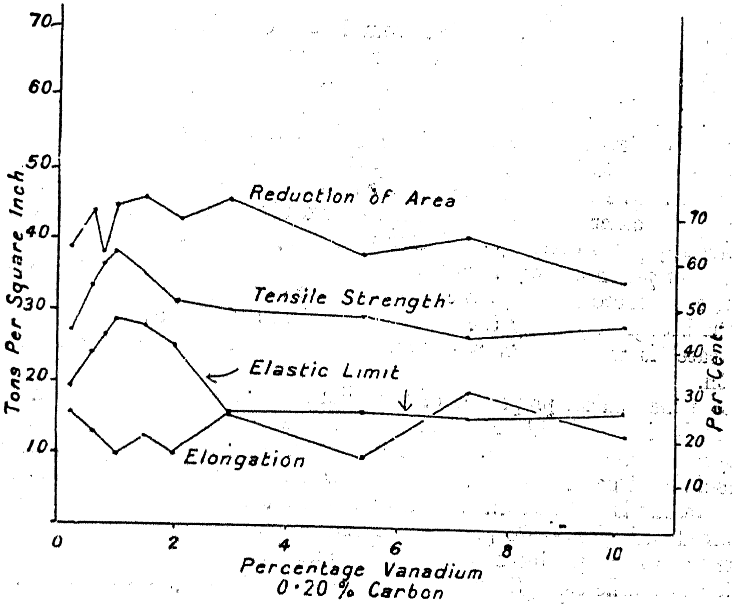
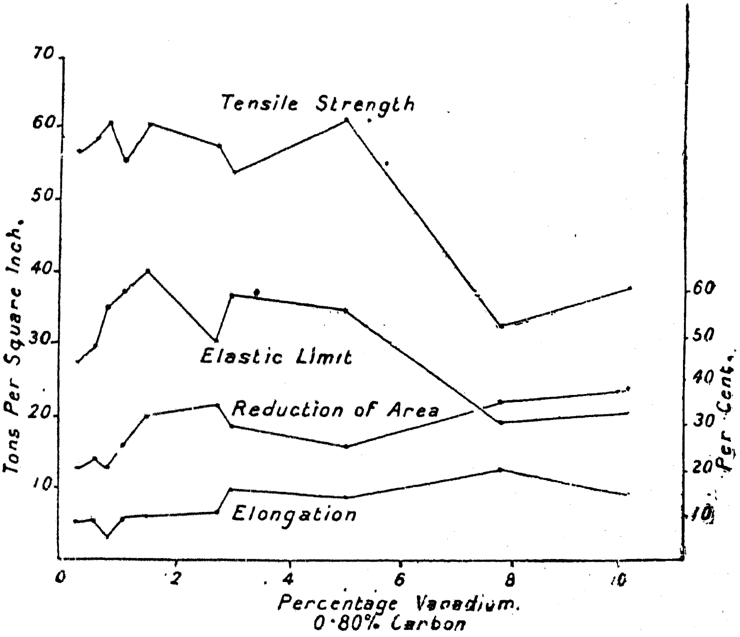

70
60
50
40
30
20
10
Tons Per Square Inch
Reduction of Area
Tensile Strength
Elastic Limit
Elongation
70
60
50
40
30
20
10
Per Cent.
0
2
4
6
8
10
Percentage Vanadium
0·20 % Carbon

Fig. 209.


70
60
50
40
30
20
10
Tons Per Square Inch.
Tensile Strength
Elastic Limit
Reduction of Area
Elongation
60
50
40
30
20
10
Per Cent.
0
2
4
6
8
10
Percentage Vanadium.
0·80% Carbon

cent. of vanadium, when cooled from 1,020° C., did not show any point corresponding to the Ar_3 change. The Ar_2 appeared at 791° C., and the Ar_1, which was very small considering the amount of carbon, occurred at 720° C. A steel with 1·07 of carbon and 10·3 of vanadium, when cooled from 1,210° C., gave no evidence of the Ar_3 or Ar_1 points, the Ar_2 appeared at 830° C. Further, this steel, when rapidly quenched from 1,050° C., was quite soft to the file. These are most remarkable facts, and are exceedingly interesting, because no other element is known to have the same effect. The absence of the Ar_1 point certainly indicates that the carbide of vanadium is only soluble in γ-iron at very high temperatures. The disappearance of the Ar_3 change, or, more correctly, the raising of the change, strongly suggests that this is brought about by the vanadium held in solid solution, and if this is the case, it would mean that vanadium is more soluble in α-iron than γ-iron.

The mechanical properties of vanadium-carbon steels have been determined by Dr. Guillet.[1] His work was carried out on two series of steels containing 0·20 and 0·80 per cent. of carbon with up to 10·0 per cent. of vanadium. The tensile properties are shown in figs. 209 and 210. From these results it will be seen that in both series the best all-round results are obtained with about 0·70 per cent. of vanadium. Increasing the percentage from 0·0 to 0·7 produces a progressive and substantial rise in the elastic limit and tensile strength, which is also accompanied by an increase in the ductility of the steel.

---

[1] *Revue de Metallurgie*, 1905, p. 525.

CHAPTER XXII.

STRUCTURAL CONSTITUTION OF SPECIAL TERNARY STEELS.

In the chapter dealing with the microstructure of carbon steels a detailed description has been given of the structural constituents and appearances which are known as ferrite, pearlite, sorbitic pearlite, troostitic pearlite, cementite, martensite, and austenite. Since these are the constituents and structures which are also met with in the treatment of special steels, it will be advantageous once again to refer briefly to the conditions and treatment under which they are formed in carbon steels.

Ferrite.—This constituent is present in the massive crystalline condition in all slowly-cooled steels containing less than 0·89 per cent. of carbon. As a rule, it is almost pure iron, but it may sometimes contain notable quantities of impurities in solid solution. It is relatively very soft and magnetic.

Pearlite.—Is an intimate mixture of crystallised α-iron and carbide of iron which have crystallised at the same time from the solid solution of the eutectoid composition. It, therefore, contains 0·89 per cent. of carbon, and is obtained by slow cooling.

Sorbitic pearlite is very similar in many ways to ordinary pearlite, but it is in a finer state of division, owing to the fact that it is obtained by moderately quick cooling from about 700° C., which prevents the normal crystallisation into ordinary pearlite.

Troostitic pearlite or troostite is an exceedingly fine mixture of carbide of iron and ferrite, which has the same composition as pearlite. It is formed from the same solid solution as pearlite, but is only obtained in carbon steels by very rapid cooling, such as quenching, at the time the solid solution is decomposing into its constituents.

Cementite.—Carbide of iron (Fe_3C) occurs in all slowly-cooled steels as a constituent of pearlite, and in the free or massive form in slowly-cooled steels containing more than 0·89 per cent. of carbon. It is hard and brittle.

Martensite is obtained by quenching all steels from temperatures above their highest recalescence points. It is exceedingly hard when it contains 0·89 per cent. of carbon, but is considerably softer when the carbon content decreases. Martensite can only be obtained in carbon steels by very rapid cooling, and, therefore, the proportion of the steel which can be kept in this state decreases as the size of specimens increases, because of the diminished rate of cooling.

Austenite.—Obtained by rapidly quenching steels with 1·0 to 1·65 per cent. of carbon from above 1,000° C. in ice-cold water. Under the most favourable conditions not more than about 35 per cent. of a carbon steel can be preserved in this state. It is softer than martensite.

The above constituents are all found in almost every series of special steels, but, owing to the presence of a third element, the conditions under which they are obtained may differ entirely from those of carbon steels. This difference is due to the effect of the third element upon the temperature at which the ordinary critical points of carbon steels occur. If the added element lowers the temperature of the critical points, and especially that of the Ar_1 change, its action will be in the same direction as that of quenching, which also lowers the temperature of the Ar_1 point. When lowering of the transformation points occur, whether it is produced by rapid cooling in carbon steels or by a third element with very slow rates of cooling, the effect upon the mechanical properties will be very similar, providing the change occurs at the same temperature in each case

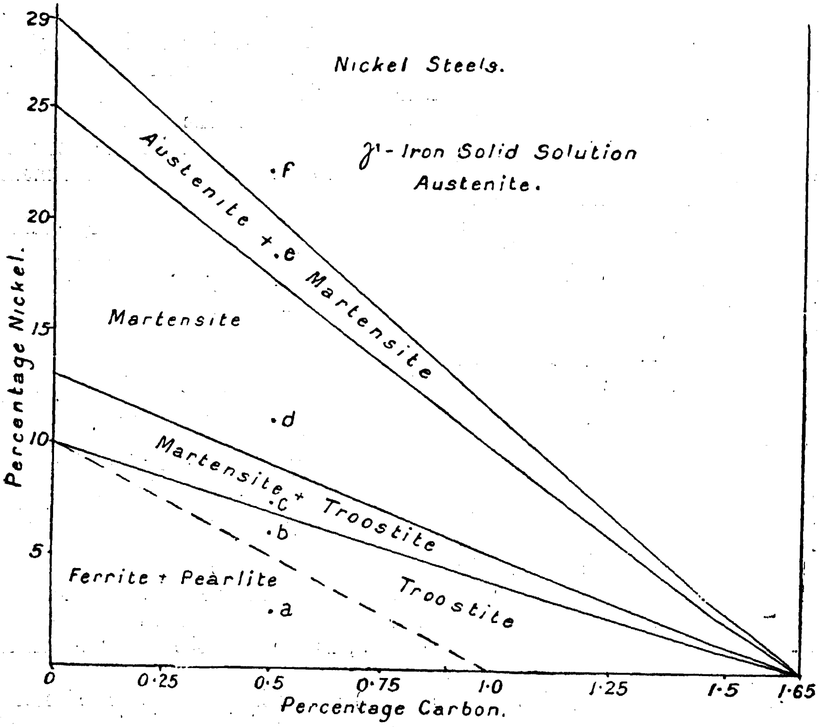


Fig. 211.

It is evident that when a certain percentage of a third element is capable of lowering the temperature of the critical points below that of the ordinary atmosphere, the temperature of those points can be easily controlled for any given rate of cooling simply by selecting the correct percentage of the third element. Any lowering of, for instance, the carbide Ar_1 change naturally means that the mass of steel has a narrower range of temperature over which the carbide and ferrite, which then separates from the pre-existing solid solution, can coalesce or crystallise. Hence the crystals of ferrite and cementite contained in the steel are progressively smaller the lower the temperature at which they separate from the solid solution. It, therefore, follows that, by using an element such as nickel, which has a pronounced lowering effect upon the Ar_1 and other changes, very fine or sorbitic pearlite will be obtained with a certain percentage of that element, and that by increasing quantities troostite, martensite, and even the normal γ-iron solid solution can be produced even when the cooling is slow. Thus, a steel with 0·90 per cent. of carbon and 7·0 per cent. of nickel is martensitic after very slow cooling, and possesses similar properties to a quenched martensitic carbon steel. Broadly speaking, this similarity exists in other cases, though it must be remembered that differences do occur as a result of the direct influence of the added element.

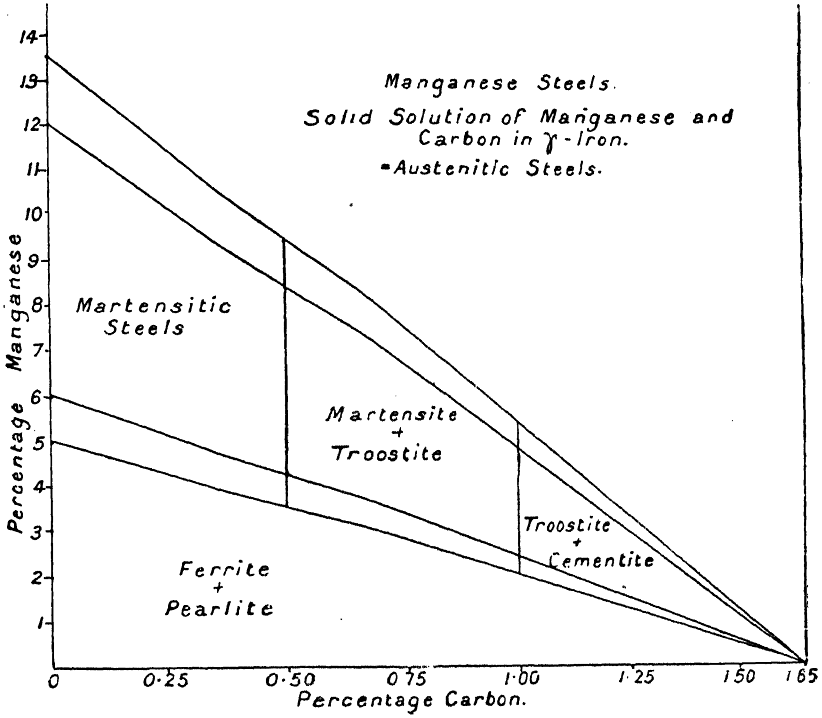


Fig. 212.

Dr. Guillet has made very careful microscopic examinations of almost all the special ternary steels, and has illustrated his results in what may provisionally be described as constitutional diagrams. These are shown in figs. 205 to 214, and are very useful in making a study of the various kinds of ternary steels. After describing one of these the others will be readily understood. The constitution of nickel steels is represented in fig. 211. In this diagram the horizontal ordinates represent the percentages of carbon,

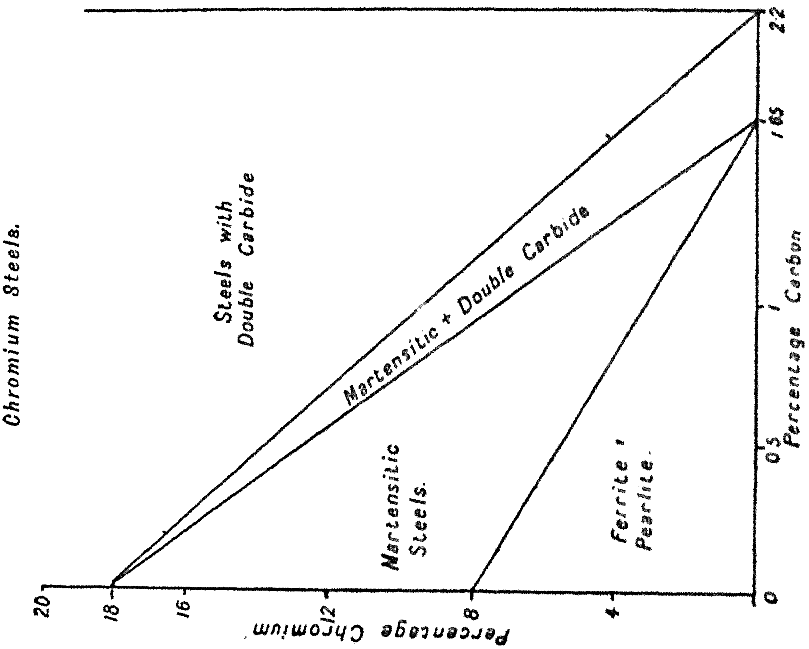


Fig. 213.

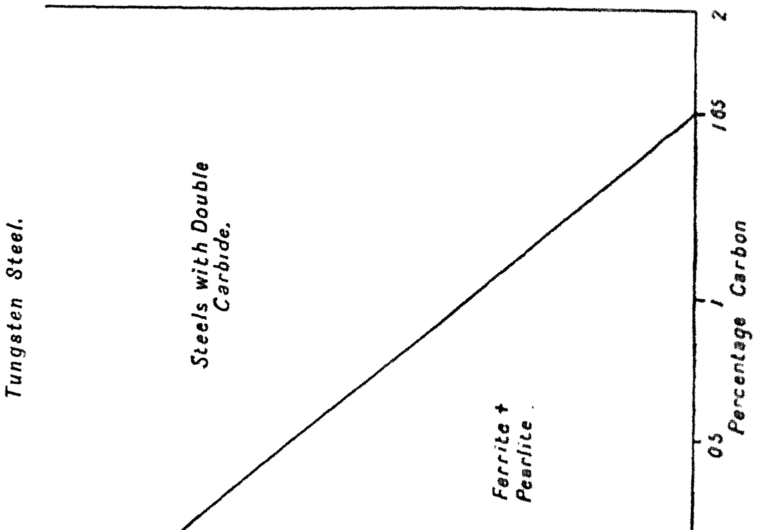


Fig. 214.

and the vertical ordinates those of nickel. A slowly-cooled steel corresponding in composition to a point inside any of the areas illustrated in the diagram will have the structural constitution referred to in that area. This will be more fully understood by considering a series of steels containing a constant percentage of carbon with varying nickel content. Considering a series with 0·5 per cent. of carbon and *a*, *b*, *c*, *d*, *e*, and *f* of nickel, they will show when viewed under the microscope the following structures :—

a = 2·5 per cent. of nickel = ferrite + pearlite.
b = 6·0 ,, ,, = troostite + carbide.
c = 7·5 ,, ,, = martensite + troostite.
d = 11·0 ,, ,, = martensite.
e = 18·5 ,, ,, = austenite + martensite.
f = 22·0 ,, ,, = austenite.

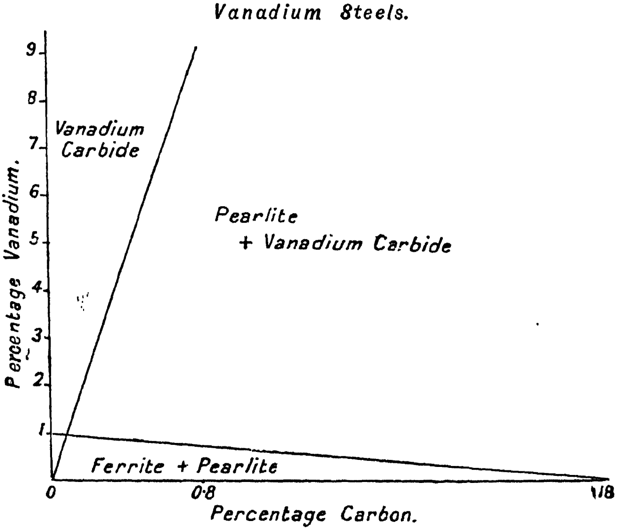

Vanadium Steels.

Fig. 215.

The effect of carbon can be ascertained in a similar manner by considering a series with a constant percentage of nickel. It should be noted that, whilst the various members of any particular group possess the same constitution owing to the wide variation in their composition, the constituents are seen under different conditions, or, in other words, their degree of fineness or coarseness varies on passing from one side of the area to the other. It is also necessary to point out that the meeting of the areas, austentite, martensite, troostite, etc., at the 1·65 per cent. carbon point may be regarded as somewhat arbitrary. Dr. Guillet has chosen this percentage, because it is supposed that with ideal rates of quenching for a steel containing 1·65 per cent. of carbon the mass would be retained in the state of non-magnetic γ-iron solid solution.

On comparing the constitution of manganese steels (fig. 212) with fig. 21 it will be observed that about 13·5 per cent. of manganese has the sam effect in preserving the iron in γ condition as 29 per cent. of nickel, or tha the ratio is 1 : 2·14. This means that 1·0 of manganese has the same effec in modifying the structure of steel as 2·14 of nickel, but it does not follo that the mechanical properties of such steels will be the same. They ma possess many similarities in this respect, but there are also marked differences

CHAPTER XXIII.

ELECTRICAL CONDUCTIVITY AND CONSTITUTION.

The study of the electrical conductivity of metals and their alloys at varying temperatures, and after different mechanical and heat-treatment has been undertaken by a large number of investigators. Whilst many of these have been conducted from the point of view of the physicist or electrical engineer, they have substantially contributed to our knowledge of the inner structure and constitution of metallic alloys, and are, therefore, of considerable direct interest to metallurgists. The examination of the influence of treatment and composition of alloys upon their electrical conductivity has indeed now become one of the metallurgists' standard methods of investigation. For certain metallographical purposes this method is even more delicate than that of a thermal or microscopical examination. This is more especially the case when we come to consider some of the more subtle changes which may take place when such constituents as solid solutions are heated or cooled. Under these conditions changes of a progressive nature may occur, such as the decomposition of a compound into its constituents, or depolymerisation of a compound that is held in solid solution. Transformations of this kind will not give rise to any well defined thermal disturbance, and the internal rearrangement would naturally be of molecular dimensions, and consequently far beyond the powers of the microscope. Still there are good reasons for believing that progressive changes of this kind often take place in alloys, and equally good grounds for considering that they exert a profound influence upon the physical properties of the mass.

For the purest metals it is known that for all but the very lowest temperatures the conductivity is inversely proportional to the absolute temperature. For exceedingly low temperatures, approximately those of liquid helium, the resistance in certain cases is almost zero. Therefore, the resistance falls almost in proportion to the fall in temperature until a certain low critical temperature is reached after which the decrease in resistance becomes very much more rapid.

The transport of electricity through metals is explained by Sir J. J. Thompson[1] as follows :—

" We will suppose that each atom of the metal contains an electrical dipole—the electrical analogue of the molecular magnet. The molecular magnet consists of equal and opposite magnetic poles separated by a short distance. The electrical dipole consists of equal and opposite electrical charges at a short distance apart, the negative charge being an electron. These dipoles, if acted upon by an electrical force, will set themselves along the lines of electric force in the same fashion as the magnets along the lines of magnetic force ; the result will be the same as if a certain fraction pointed

[1] " May Lecture," Institute of Metals, 195, vol. ii.

in the direction of the electric force, while the remainder pointed indifferently in all directions. We thus shall have in the substance a number of chains of atoms. . . . The doublets in the atoms will produce intense electric forces in their neighbourhood, and these forces will tend to drag the electrons out of one atom into the other. The force which drags the electrons out is due to the pull exerted by the atoms in its neighbourhood, and so does not depend on the magnitude of the electric force." In the course of the lecture this view is developed, and a mathematical explanation is given for the very rapid increase in the conductivity that occurs when metals are cooled below certain low critical temperatures.

It seems highly probable that, with some slight modification, Sir J. J. Thompson's views in this connection might provide the explanation of the peculiarly rapid decrease in the electrical conductivity which occurs when small quantities of an element are held in solid solution by a metal, and the relatively much smaller decrease which takes place (per unit of added element) when larger quantities of the same substance are in solution.

As regards the electrical resistivity of iron the lowest values which have been experimentally determined are from 9·0 to 9·7 microhms per cm^3. It is, however, necessary to note that exceedingly small quantities of certain impurities present in iron or even in any other metal have a marked effect upon the conductivity, and this fact makes it extremely difficult to obtain a reliable experimental value for the pure metal. Benedicks, who has given considerable attention to this matter, by extrapolation, evaluates the electrical resistance of the pure metal iron at 7·6 microhms per cm^3. This figure is considerably lower than the lowest that has been observed, but, as indicated by Benedicks,[1] if we take the figure of 9·7 microhms per cm.^{3} obtained by W. H. Preece,[2] the difference between this and the theoretical figure would be accounted for by the presence of 0·007 per cent. of hydrogen in the metal.

Among the more important papers dealing with the resistance of iron and steel at high temperatures are those by J. Hopkinson,[3] H. Le Chatelier,[4] and Boudouard.[5] The last investigator finds that the curve depicting the electrical resistance of iron and of steels does not lose its parabolic form between the ordinary temperature and that at which the thermal transformations begin to occur. But from 800° C. onwards they become linear. For carbon steels the following equations represent the facts above 800° C.:—

Steel with 0·205 per cent. carbon, . . . $R = 42{\cdot}8 + {\cdot}0846t$.
" 0·493 " . . . $R = 47{\cdot}0 + {\cdot}043t$.
" 0·841 " . . . $R = 72{\cdot}7 + {\cdot}023t$.
" 0·82 " . . . $R = 92{\cdot}9 + {\cdot}028t$.
" 1·05 " . . . $R = 92{\cdot}0 + {\cdot}029t$.
" 1·16 " . . . $R = 90{\cdot}6 + {\cdot}0283t$.
" 1·38 " . . . $R = 97{\cdot}75 + {\cdot}0301t$

In the case of the specimen of iron which Boudouard examined the three following linear equations are given as corresponding with the results:—

---

[1] "Thèse pour le Doctorat," Upsala, 1904.
[2] Report British Assoc., Manchester, 1887, p. 609.
[3] *Phil. Trans.*, 180: 1 (1889), p. 443.
[4] *Comptes Rendus*, 126 (1898), pp. 1709, 1782.
[5] *Journ. Iron and Steel Inst.*, 1903, i., p. 299.

From 655° C. to 775° C., . . $R = -51{\cdot}9 + 0{\cdot}189t$.
From 781° C. to 875° C., ... $R = 39{\cdot}3 + {\cdot}071t$.
From 896° C. to 1,170° C., ... $R = 74{\cdot}4 + {\cdot}031t$.

Burgess and Kellberg[1] have examined the resistance of pure iro temperatures between 0° and 950° C. The results show that the resist of iron increases at a gradually increasing rate until the neighbourhoc the first critical region (A_2) is reached. This region is characterised point of inflection on the resistance temperature curve at 757°. Wi further increase of temperature an abrupt fall in the resistance occu about 894° C., and the reverse change takes place at approximately same temperature when the temperature is allowed to fall. This se critical region (A_3) extends over an interval of 25° C.

A great number of investigations have been made on the electrica sistance of alloys, at the ordinary temperature, in relation to the che composition and structural constitution. Amongst these should be menti those by Matthiessen,[2] Johnson,[3] Hopkinson,[4] Osmond,[5] Stead,[6] Ebe Mathews,[8] and, more especially, those by Le Chatelier,[9] Barrett, Br and Hadfield,[10] Barns and Strouhal,[11] Benedicks,[12] Campbell,[13] Swinc Maurer,[15] Portevin,[16] Fournel,[17] and Saldau.[18]

The results of Fournel's investigations are embodied in Table XLVII.

TABLE XLVII.

Composition.			Transformation Point.			Formulæ of the Straight Line Increase of the Electric Resista at Temperature above 900° C
C	Si	Mu	Ar_3	Ar_2	Ar_1	
·08	·24	·43	880	775	..	R*t* = R900 (1 + 3·3 × 10–
·11	·02	·35	890	780	670	R*t* = R900 (1 + 3·3 × 10–
·22	·33	·57	790	740	695	R*t* = R900 (1 + 4·3 × 10–
·37	·126	·47		730-770		R*t* = R900 (1 + 3·8 × 10–
1·05	?	·25		730-770		R*t* = R900 (1 + 4·0 × 10–

---

[1] *Journ. of the Washington Academy of Science*, 1914, vol. iv., pp. 436-440.

[2] *Phil. Trans.*, 1858, 148, 383; 1860, 150, 161. *Phil. Mag.*, 1861 (iv.), 21, 107; 22, 195. Matthiessen and Vogt, *Phil. Trans.*, 1864, 154, 167. *Phil. Mag.*, 1862 23, 171.

[3] *Chemical News*, vol. xliv., 1881, p. 178. [4] *Phil. Trans.*, 1889, vol. clxxx.,

[5] " Rapport de la Commission des Méthodes d'Essais des Matériaux de Construc Oct. 1892.

[6] *Journ. Iron and Steel Inst.*, 1895, No. 1, p. 77.

[7] *Zeit für Instrumentenkunde*, vol. xvi., 1896, p. 87.

[8] " Metallic Conduction and the Constitution of Alloys."

[9] *Comptes Rendus*, vol. cxxvi., 1898, pp. 1709, 1782. *Contribution à l'Étu Alliages*, 1901, p. 316.

[10] *Scientific Transactions of the Royal Dublin Society*, vol. viii., (2) 1902, p. 1.

[11] *Bulletin of the United States Geological Survey*, vol. ii., 1885, p. 593.

[12] *Thèse pour le Doctorat*, Upsala.

[13] *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 164.

[14] *Journ. Iron and Steel Inst.*, 1909, No. 2, p. 223.

[15] *Revue de Métallurgie*, vol. v., 1908, p. 711.

[16] *Iron and Steel Inst. Carnegie Research Memoirs*, **1909**.

[17] *Comptes Rendus*, 1906, vol. 143, pp. 46, 287.

[18] *Carnegie Memoir Iron and Steel Inst.*, 1916, vol. vii., p. 195.

From 655° C. to 775° C., . . $R = -51{\cdot}9 + 0{\cdot}189t$.
From 781° C. to 875° C., ... $R = 39{\cdot}3 + {\cdot}071t$.
From 896° C. to 1,170° C., ... $R = 74{\cdot}4 + {\cdot}031t$.

Burgess and Kellberg[1] have examined the resistance of pure iron at temperatures between 0° and 950° C. The results show that the resistance of iron increases at a gradually increasing rate until the neighbourhood of the first critical region (A_2) is reached. This region is characterised by a point of inflection on the resistance temperature curve at 757°. With a further increase of temperature an abrupt fall in the resistance occurs at about 894° C., and the reverse change takes place at approximately the same temperature when the temperature is allowed to fall. This second critical region (A_3) extends over an interval of 25° C.

A great number of investigations have been made on the electrical resistance of alloys, at the ordinary temperature, in relation to the chemical composition and structural constitution. Amongst these should be mentioned those by Matthiessen,[2] Johnson,[3] Hopkinson,[4] Osmond,[5] Stead,[6] Ebeling,[7] Mathews,[8] and, more especially, those by Le Chatelier,[9] Barrett, Brown, and Hadfield,[10] Barns and Strouhal,[11] Benedicks,[12] Campbell,[13] Swinden,[14] Maurer,[15] Portevin,[16] Fournel,[17] and Saldau.[18]

The results of Fournel's investigations are embodied in Table XLVII.

TABLE XLVII.

Composition.			Transformation Point.			Formulæ of the Straight Line Increase of the Electric Resistance at Temperature above 900° C.
C	Si	Mu	Ar_3	Ar_2	Ar_1	
·08	·24	·43	880	775	..	$Rt = R900\,(1 + 3{\cdot}3 \times 10^{-4}\,t)$
·11	·02	·35	890	780	670	$Rt = R900\,(1 + 3{\cdot}3 \times 10^{-4}\,t)$
·22	·33	·57	790	740	695	$Rt = R900\,(1 + 4{\cdot}3 \times 10^{-4}\,t)$
·37	·126	·47	730-770			$Rt = R900\,(1 + 3{\cdot}8 \times 10^{-4}\,t)$
1·05	?	·25	730-770			$Rt = R900\,(1 + 4{\cdot}0 \times 10^{-4}\,t)$

---

[1] *Journ. of the Washington Academy of Science*, 1914, vol. iv., pp. 436-440.

[2] *Phil. Trans.*, 1858, 148, 383; 1860, 150, 161. *Phil. Mag.*, 1861 (iv.), 21, 107; (iv.), 22, 195. Matthiessen and Vogt, *Phil. Trans.*, 1864, 154, 167. *Phil. Mag.*, 1862 (iv.), 23, 171.

[3] *Chemical News*, vol. xliv., 1881, p. 178. [4] *Phil. Trans.*, 1889, vol. clxxx., p. 443.

[5] "Rapport de la Commission des Méthodes d'Essais des Matériaux de Construction," Oct. 1892.

[6] *Journ. Iron and Steel Inst.*, 1895, No. 1, p. 77.

[7] *Zeit für Instrumentenkunde*, vol. xvi., 1896, p. 87.

[8] "Metallic Conduction and the Constitution of Alloys."

[9] *Comptes Rendus*, vol. cxxvi., 1898, pp. 1709, 1782. *Contribution à l'Étude des Alliages*, 1901, p. 316.

[10] *Scientific Transactions of the Royal Dublin Society*, vol. viii., (2) 1902, p. 1.

[11] *Bulletin of the United States Geological Survey*, vol. ii., 1885, p. 593.

[12] *Thèse pour le Doctorat*, Upsala.

[13] *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 164.

[14] *Journ. Iron and Steel Inst.*, 1909, No. 2, p. 223.

[15] *Revue de Métallurgie*, vol. v., 1908, p. 711.

[16] *Iron and Steel Inst. Carnegie Research Memoirs*, 1909.

[17] *Comptes Rendus*, 1906, vol. 143, pp. 46, 287.

[18] *Carnegie Memoir Iron and Steel Inst.*, 1916, vol. vii., p. 195.

Fournel concluded that the rise in the electrical resistance at temperatures above 900° C. proceeds in accordance with the straight line formula $Rt = R\,900\,(1 + at)$ in which a varies for the different steels.

Saldau has made an extremely valuable series of determination of the electrical resistance of Kahlbaum iron and carbon steels at temperatures up to 1,100° C. The results for iron are given in Table XLVIII., and plotted in fig. 216.

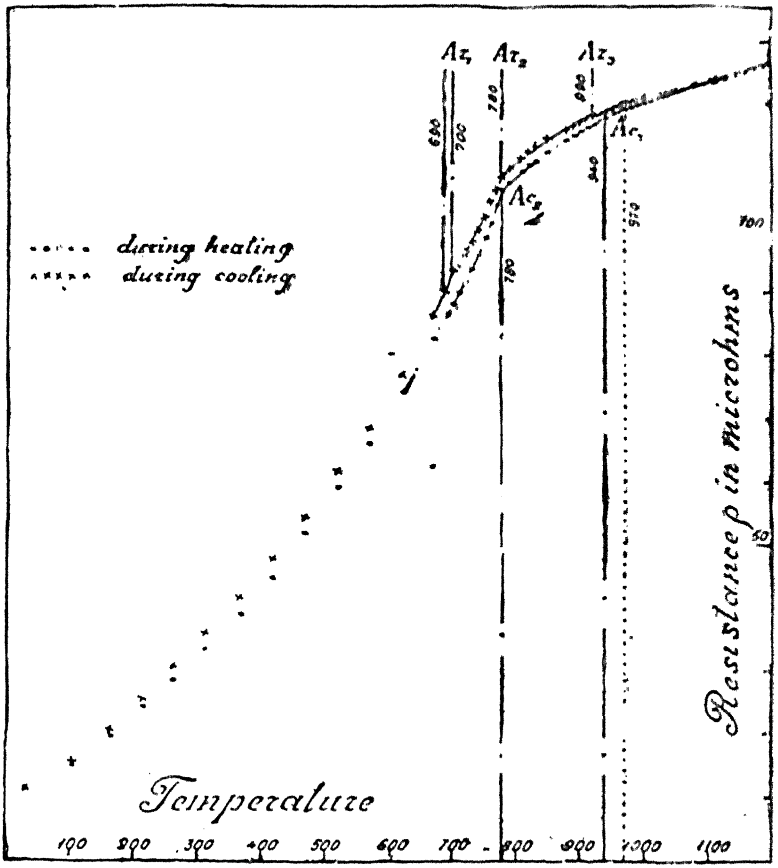


Fig. 216.—Kahlbaum Iron (the First Heating in the Nitrogen Gas).

As the total impurities in this iron was only ·047 per cent., consisting of carbon, ·019; manganese, ·025; silicon, ·006; phosphorus, ·012; and sulphur, ·004 per cent., and the determinations were made in an atmosphere of nitrogen, this data is probably the most reliable so far obtained. The electrical resistances of the various carbon steels, after being hardened from

800° C., 900° C., and 950° C., are plotted in fig. 217. From these curves it will be seen that the resistivity of the sample containing ·89 per cent. of

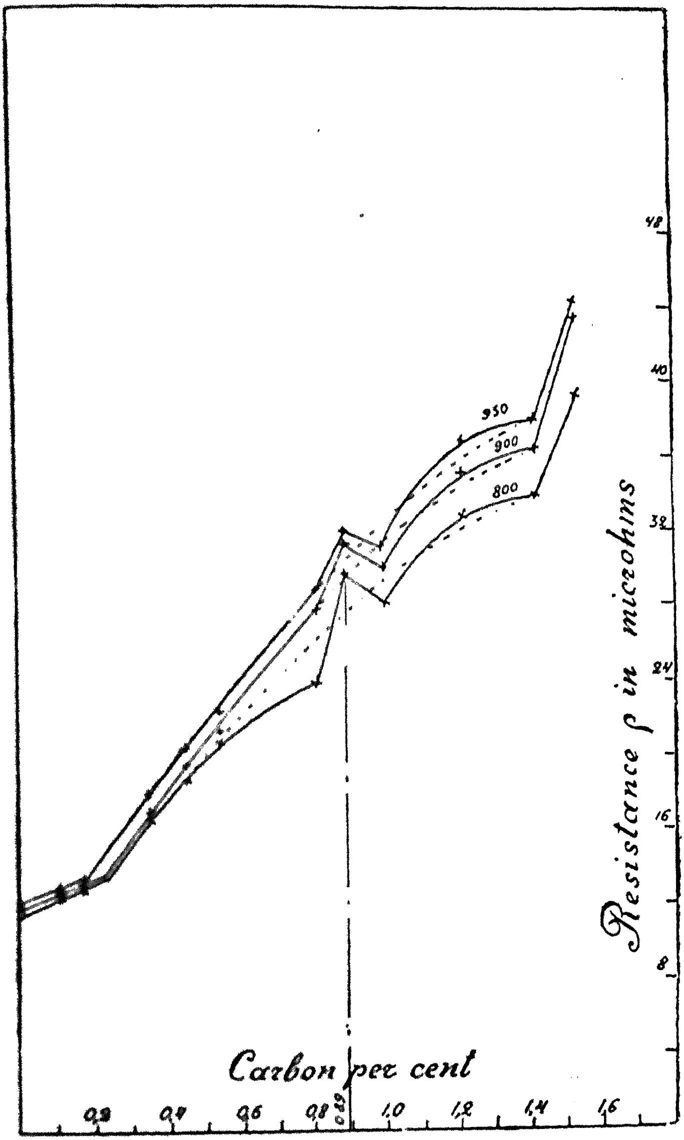


Fig. 217.—Curves of the Electric Resistance of Iron and Steel after Heating.

carbon is relatively higher than the samples on either side of that composition.

TABLE XLVIII.

Temperature.	Kahlbaum Iron.				Temperature.	Kahlbaum Iron.			
	Resistance, $\rho \times 10^6$.		Conductivity, $K=\frac{1}{\rho}\times 10^{-4}$.			Resistance, $\rho \times 10^6$.		Conductivity, $K=\frac{1}{\rho}\times 10^{-4}$.	
	During Heating.	During Cooling.	During Heating.	During Cooling.		During Heating.	During Cooling.	During Heating.	During Cooling.
25	10·457	10·920	9·563	9·158	760	98·855	104·260	1·012	0·959
100	15·084	15·846	6·630	6·311	770	101·380	106·330	0·986	0·941
150	17·737	19·893	5·638	5·027	780	104·350	109·130	0·958	0·917
200	20·978	24·310	4·767	4·114	790	105·520	110·470	0·948	0·905
250	25·210	28·270	3·967	3·537	800	106·600	111·730	0·938	0·895
300	29·800	32·772	3·356	3·051	850	111·910	116·410	0·894	0·859
350	34·933	38·354	2·863	2·607	880	114·880	118·580	0·870	0·843
400	41·236	44·116	2·425	2·267	890	115·960	119·110	0·862	0·840
450	47·988	50·508	2·084	1·980	900	117·040	119·650	0·854	0·836
500	54·740	57·621	1·827	1·735	910	118·120	120·100	0·847	0·833
550	62·123	64·374	1·610	1·553	920	119·200	120·660	0·839	0·829
600	70·225	72·027	1·424	1·388	930	120·200	121·000	0·832	0·826
650	78·510	80·850	1·274	1·236	940	121·100	121·270	0·826	0·825
680	83·550	85·712	1·197	1·167	950	121·360	121·540	0·824	0·823
690	85·442	87·692	1·170	1·140	980	122·170	122·260	0·819	0·818
700	87·152	90·032	1·147	1·111	1000	122·720	122·800	0·815	0·814
710	88·862	94·265	1·125	1·061	1020	123·250	123·430	0·811	0·810
720	90·662	96·334	1·103	1·038	1050	124·060	124·430	0·806	0·804
730	92·464	98·315	1·082	1·017	1080	124·880	125·300	0·801	0·798
740	94·445	100·300	1·059	0·997	1100	125·420	..	0·797	..
750	96·514	102·280	1·036	0·978					

The relations between conductivity and constitution have been specially studied by Le Chatelier, *loc. cit.* The researches of this investigator enabled him to subdivide alloys into three general groups according to their structural constitution. The laws he enunciated may be described as follows :—

1*st Group.*—Alloys in which the components are mutually insoluble in each other in the solid state.

In systems of this kind the electrical conductivity is a linear function of the volume concentration of the two components. Guertler[1] has shown that this law is sometimes not strictly correct, for the conductivity may be seriously influenced by the manner in which the separate constituents are distributed throughout the mass. For example, in the case of the copper-bismuth alloys which fall into this group as regards constitution, the conductivity is very far from being a linear function of the volume concentration. In this instance, with the addition of comparatively small quantities of bismuth, the conductivity rapidly falls to the value for bismuth. This, however, is due to the fact that the crystals of copper become completely surrounded by bismuth, and when this occurs the resistance of the mass is ually governed by that of the element which exists at the boundaries he crystals.

---

[1] *Zeit. für anorganische Chemie*, 51 (1906), 397 ; 54 (1907), 58.

2nd *Group.*—Alloys in which are formed a continuous series of solid itions from one end of the system to the other.

The conductivity curve of alloys belonging to this group takes a U-shaped n, showing that the effect of adding either one of the elements to the other rst to produce a very rapid decrease in the conductivity which continues il a certain limiting and comparatively low percentage of the added nent is reached, after which further additions produce a lowering of the ve which is infinitely less than was first obtained.

3*rd Group.*—Alloys in which there is a limiting range of solid solutions ach end of the system. In this case the same rapid fall in conductivity ound at each end of the diagram as for those mixtures in group 2, with raight line from the points corresponding with the saturation limits of two solid solutions.

The Influence of other Elements upon the Electrical Resistance of Iron.— m a consideration of the data previously published and experimental lence obtained by himself, Benedicks has shown that the resistivity ron depends upon the amount of impurity held in solid solution by the . Further, he advanced the theory that the influence of an impurity the resistivity followed a definite law, and was inversely proportional he atomic weight of the dissolved element. That is to say, equi-atomic tions of different impurities have the same electrical resistance. This holds for a very wide variety of steels containing carbon, aluminium, on, phosphorus, chromium, manganese, cobalt, nickel, arsenic, molybum, and tungsten, elements which vary in atomic weight fron 12 to 184.

Benedicks' formula, expressing the resistance of steel at the ordinary perature, is :—

$$R = 7{\cdot}6 + 26{\cdot}8\ \Sigma\ C \text{ microhms per cm}^3,$$

re Σ C is the " carbon value " of the amount of the element present, ch is found as follows :—

$$\Sigma\ C = C + \frac{12{\cdot}0}{28{\cdot}4}\,Si + \frac{12{\cdot}0}{55}\,Mn + \frac{12}{27{\cdot}1}\,Al + \ \ldots$$

According to this equation we find that 1 atom of an element dissolved 00 atoms of iron increases the resistance of iron by 5·9 microhms per . Benedicks states that it is difficult to fix the upper limit of comtion to which the above formula can be applied, but that it is probably ter than Σ C = 2·0 per cent., and less than 3·0 per cent. Or, in other ds, it will probably not be applicable to concentrations greater than tom dissolved in 8 atoms of iron. This is exactly what would be cipated from what is known regarding the relationship between revity and solid solutions (see Le Chatelier's 2nd law) which indicates Benedicks' formula applies to the steep branches of the U-shaped contivity curve. For special alloy steels Portevin[1] has shown that the ve formula is inapplicable if the carbon equivalent of all elements, other 1 iron, exceeds 2 or 3 per cent.

---

[1] *Journ. Iron and Steel Inst. Carnegie Memoir*, No. 1, 1909.

An examination of the figures given in Table XLIX., which is taken from Benedicks' paper, indicates how closely the values calculated by means of the above equation agree with those that have been experimentally determined. The letter *q* means that the samples have been quenched.

TABLE XLIX.

Elements in Solution.					Electrical Resistance Microhms per Cm³.	
Carbon as Cementite.	Carbon in Solution.	Silicon in terms of Carbon.	Manganese in terms of Carbon.	Σ C.	Determined Resistance.	Calculated Resistance.
..	·08	·013	·028	·121	10·5	10·8
.. *q*	·08	·013	·028	·121	10·9	10·8
1·43	·27	·034	·063	·367	17·7	17·4
1·23	·27	·051	·063	·384	17·9	17·9
0·63	·27	·118	·089	·477	20·2	20·4
0·93	·27	·127	·096	·493	20·9	20·8
1·08	·27	·110	·118	·498	21·6	21·0
0·18	·27	·274	·076	·620	23·9	24·2
0·28	·27	·363	·096	·729	27·6	27·2
.. *q*	·45	·274	·076	·800	29·0	29·0
.. *q*	·55	·363	·096	1·009	34·4	34·6
.. *q*	·90	·118	·089	1·107	36·9	37·3
(0·13) *q*	1·20	·127	·096	1·423	42·1	(45·7)
(0·21) *q*	1·35	·110	·118	1·578	44·4	(49·6)
.. *q*	1·35	·110	·118	1·578	49·6	49·6
.. *q*	1·50	·051	·063	1·614	50·6	50·8

It is by means of extrapolating this and other similar data that Benedicks has evolved the theoretical resistance of 7·6 microhms per cm³ for pure iron. Even in annealed carbon steels Benedicks considers that when the total carbon is above ·5 per cent., the ferrite holds approximately ·27 per cent. of carbon in solid solution. This interesting conclusion, which is supported by the resistivity determinations, would appear to indicate that the ferrite which is deposited directly from the gamma-solid solution as alpha-iron will more readily hold carbon in solution than when it is formed as a result of the $\beta = \alpha$ transportation.

It is by pressing forward research along lines similar to those suggested by Benedicks' work that we may hope to arrive at a much better conception of the nature of solid solutions and the changes which they undergo when heated. This is a most fascinating theoretical subject, and, moreover, as steel consists of solid solutions during the larger part of the time they are being rolled, forged, or heat treated, any advance which can be made in this direction should be advantageous to steel users.

From physico-chemical considerations, Juptner[1] has calculated that carbon when present in steel in the form of a solid solution at temperatures of 900° C., or over, exists with the molecular formula $(Fe_3C)_2$, but that as the temperature is lowered to a point just before the Ar_1 change, it takes up the more complex form $(Fe_3C)_4$.

---

[1] *Journ. Iron and Steel Inst.*, 1898, No. I., p. 204, and 1898, No. I., p. 235.

Campbell[1] has studied this problem in quite a different way, and arrived at the same conclusion. His method was to analyse the gases which are evolved when hardened and annealed steels are dissolved in hydrochloric acid.

In this work it was found that the greater part of the carbon in annealed steels is evolved as C_4H_{10}, associated with C_3H and C_2H_6; in quenched steel the bulk of the carbon comes off as the lower member of the series. As the kind of hydrocarbon formed must have a direct relationship with the molecular complexity of the carbide in the steel, it is necessary to consider that the carbon in solid solution is present as $(Fe_3C)_2$, and that when this is deposited from solution it polymerises, giving the formula $(Fe_3C)_4$ for cementite of annealed steels.

Another argument which Campbell advances in favour of the view that the iron carbide in steel varies in molecular aggregation, is the behaviour of steel towards nitric acid. In the well-known colorimetric method for determining carbon, it is recognised that in order to obtain reliable results it is necessary that both sample and standard should have been subjected to the same heat treatment. If there were only one carbide of iron, it is hard to understand why the depth of colour obtained by dissolving in nitric acid should not be directly proportional to the carbon present.

It was also suggested by the same investigator[2] that the carbide, after first going into solution at Ac_1 as $(Fe_3C)_2$, might be further depolymerised into the simple Fe_3C as the temperature is raised to a considerably higher degree. At a still later date[3] he was able to obtain experimental evidence with regard to the electrical resistivity of a series of steels after being quenched from 892° C. and 1,103° C., which very strongly suggests, if it does not actually prove, that some kind of molecular dissociation occurs when steels are heated above the Ac_1 change. The data obtained in this way for the resistivities of the quenched and subsequently tempered samples are given in Table L.

TABLE L.—SPECIFIC RESISTANCE IN MICROHMS PER CM³.

Carbon per cent.	Quenched from 1103° C.	Quenched from 892° C.	Steel Quenched from 892° C. reheated to							
			105° C.	195° C.	205° C.	400° C.	492° C.	600° C.	700° C.	800° C.
0·04	..	11·12	10·94	10·81	10·83	10·78	10·75	10·69	10·78	10·70
0·30	16·48	16·13	15·56	14·96	13·86	13·55	13·04	12·84	12·64	13·20
0·35	18·45	17·59	16·67	16·05	15·11	14·86	14·37	14·25	14·27	14·51
0·41	20·05	18·91	17·79	16·94	15·69	15·13	14·82	14·51	14·47	14·98
0·57	23·60	22·31	19·92	17·80	16·24	15·60	15·02	14·71	14·67	15·11
0·94	..	35·95	27·97	22·40	19·42	18·37	17·60	16·65	16·19	17·23
1·04	48·43	41·92	33·02	25·73	21·82	20·62	19·92	19·60	19·03	19·08
2·71	58·73	52·59	42·65	32·49	27·41	26·17	24·94	24·21	22·57	20·82

---

[1] *Journ. Iron and Steel Inst. Metallographist*, vol. iii., p. 32, and *Journ. Iron and Steel Inst.*, 1908, iii., p. 318

[2] *Iron and Steel Inst. Journ.*, 1908, iii., p. 318.

[3] *Iron and Steel Inst. Journ.*, 1915, ii., p. 164.

It will be seen that the samples quenched from the higher temperature give a higher electrical resistance than the same steels when quenched from 892° C. The only reasonable explanation which can at present be advanced to account for this increased resistance appears to be that the carbide molecules become less complex as the temperature is raised, and that the time taken during cooling by quenching is insufficient for them to re-associate. Thus, although the chemical composition of the steel remains unaltered, heating to high temperatures increases the number of molecules in solution, and the quenching operation more or less completely fixes that condition. In the discussion on a paper by Campbell,[1] M'Cance says :—" If the molecular weight of $(Fe_3C)_N$ in solution varied with the temperature, its value at the melting point would be different from its value at Ar_3. The depression at the freezing point at once gave a method of estimating N at those temperatures, and the figures as deduced from the results of Carpenter and Keeling were given in Table LI. (the value of Q for Ar_3 was taken as $3{\cdot}2 \times 56$).

TABLE LI.

Temperature T.	Latent Heat.		$\Delta = \frac{0{\cdot}02T^2}{Q}(1-x)$.	Actual Depression. Δa	N
	Q	x			
1,505	1,120	0·48	29·1	14·3	2·03
900	179	nil.	154·0	80·0	1·93

$$x = \frac{\text{carbon in separating solid}}{\text{total carbon}}.$$

"The carbon in solution in iron between 700° and 1,500° C. had, therefore, a constant molecular weight corresponding to the formula $(Fe_3C)_2$, and thus strengthened the conclusions drawn from the examination of the electrical resistance."

In discussing Honda's paper M'Cance[2] also says :—" In steels which have the A_2 and A_3 points separate the α to γ crystalline change A_3 took place between the non-ferromagnetic α state and the γ state, and it absorbed a certain amount of heat energy. The value of that energy, Q, had been found by the following observers to be :—

Osmond, 3·8 grain calories, *Comptes Rendus*, vol. ciii., pp. 743 and 1135 ;
Stansfield, 2·86 grain calories, *Iron and Steel Journ.*, 1899, No. II., p. 169 ;
Meuthen, 3·00 grain calories, *Ferrum*, 1912, p. 1—

giving a mean value of 3·2 calories. If it were assumed that carbon in solution was diatomic, the depression of the A_3 point for a concentration of one molecule per cent. was—

$$2\,\Delta = \frac{0{\cdot}02\,T^2}{Q}. \quad \Delta = 77^\circ\ C.$$

---

[1] *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 178.
[2] *Journ. Iron and Steel Inst.*, 1915, No. 2.

"For steels in which A_2 and A_3 were merged, the α to γ crystalline change now took place between the ferromagnetic α state and the γ state, and, in addition to the above energy Q, there must be added the energy to demagnetise. If I equalled the intensity of magnetism just before the change, the heat equivalent of this magnetic energy was $Q\,(\text{mag.}) = \frac{N\,I^2}{2\,J\,D}$, where N was Weiss' constant, J Joule's equivalent, and D was the density. In calculating now the depression of the change point, a new value, Q^1, must be used, which was the sum of Q and Q (mag.). The value of the latter was given in the table below.

TABLE LII.

Temp.	Intensity.	Q (mag).	Q^1	Depression (Δ).
752	200	0·23	3·4	55°
742	400	0·93	4·1	45°
732	600	2·10	5·3	34°
716	800	3·74	6·9	25°
700	920	4·95	8·1	21°

"On these assumptions a theoretical diagram could be drawn which was shown in fig. 218, and experimental results were placed on the same diagram to show that they were evenly distributed on both sides of the curve."

It is quite possible that the views held by Campbell and M'Cance are both fundamentally correct, and that at temperatures between, say, 700° and 900° C. the carbon is present as carbide in the form $(Fe_3C)_2$, and that as the temperature is raised this carbide first dissociates into Fe_3C, as $(Fe_3C)_2 = 2Fe_3C$, and when this reaction is completed the carbide, Fe_3C, is decomposed as follows:—$2Fe_3C = 6Fe + C_2$. The latter reaction being quite complete by the time the metal is liquid.

Working in an entirely different direction, Greenwood, Kikkawa, and the author[1] obtained certain results with a chromium steel which only appear to be explicable on the grounds that some kind of molecular dissociation occurs at high temperatures. These relate to the influence of varying initial temperatures upon the critical cooling velocities of a steel containing 6·15 per cent. of chromium and ·63 per cent. of carbon. It was found that when this steel was heated to and cooled from 900° C. the critical cooling rate—*i.e.*, the rate at which the carbide change just begins to be suppressed over the range of temperature 836° C. to 546° C.—was a little less than six minutes; but when the initial temperature was raised to 1,200° C., the critical cooling rate, again measured from 836 to 546° C., was nearly 13 minutes. Tentatively, the authors suggested that the observed differences were due to the chromium carbide first going into solution at the Ac_1 as $(Cr_3C_2)_2$, and that this carbide is progressively dissociated into Cr_3C_2 as the temperature is raised. When the steel is again cooling these molecules only slowly re-associate, and thus the molecular effect of the dissolved chromium carbide is greater as the initial temperature and molecular dissociation increase. This increased number of molecules in solution then enable the carbide point to be more readily suppressed. In an interesting investigation on the magnetic change points of chromium-carbon steels, Talnejiro Muralsami,[1] whilst accepting the idea that dissociation occurs in these steels as the temperature is raised in the solid solution range, considers that the reaction which takes place is expressed by the equation :—

---

[1] *Journ. Iron and Steel Inst.*, 1915, No. 2, p. 114.

$$2Cr_4C = Cr_3C_2 + 5Cr.$$

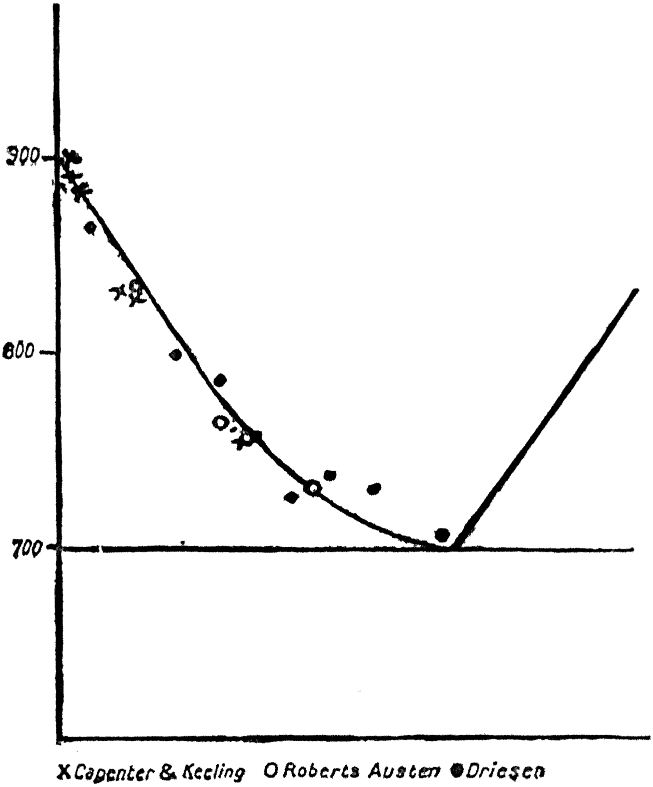


Fig. 218.

It seems very probable that the exact kind of reaction which occurs in these or any other series of steels can be determined by making an extensive series of resistivity observations with a wide variety of steels for each system, after being quenched from different initial temperatures. With this hope in view Mr. Norbury and the author have commenced such an investigation for chromium-carbon steels, and nickel-carbon steels. In considering a problem of this kind it is necessary to bear in mind that the electrical resistance of a steel is not only governed by the question as to whether the carbon has gone into solution when the temperature has passed the Ac_1 point, or any dissociation which may subsequently occur on further heating, but also by the rate of cooling. If the cooling rate is not sufficiently qiuck to completely prevent the separation of carbide the results obtained for resistivity would be misleading from the point of view of a theoretical discussion. In this connection it may be useful to examine the results obtained by H. Le Chatelier. Thus, with a steel containing 0·84 per cent. of carbon he obtained the following results :—

---

[1] *Science Reports of the Tôhoku Imperial University*, vol. vii., No. 3, p. 217.

Quenching temperature,	710°	740°	810°	850°	1,000°.
$\frac{\text{Resistance before quenching}}{\text{Resistance after quenching}} =$	1·0	1·3	2·1	2·2	2·2.

From these figures it may be concluded that it is not until the quenching temperature of 810° C. has been reached that the carbon is retained in solution under the conditions of quenching that were used. Further, even though the temperature may be above the Ac_1 change, it is necessary to allow sufficient time for the carbide to be completely taken into solution.

In an exhaustive treatise on special ternary steels, Portevin[1] devotes a large section of his paper to the study of electrical resistance. Amongst other steels he has determined the resistances, in the untreated and hardened states, for the systems—nickel-carbon iron, chromium-carbon iron, and tungsten-carbon iron. As the data for these steels is so useful and complete, it is reproduced in Tables LIII. to LV., and an attempt is made to give a brief summary of Portevin's more important conclusions.

Nickel Steels.—The results for these steels are given in Table LIII. In regard to the hardened samples it should be noted that the quenching temperature was 975° C., the time of heating at that temperature, and the temperature of the quenching bath 15° C. Concerning the results for the very low carbon series, Table LIII., these may be divided into three groups—

1st. Those containing up to 10 per cent. of nickel, and which are considered to contain the structural constituents ferrite + pearlite. The resistance increases with the percentage of nickel, and further increases on hardening.

2nd. The martensitic series with 10 to 27·0 per cent. of nickel. The resistance increases slightly with the percentage of nickel, but is scarcely influenced by hardening.

3rd. With the so-called austenitic steels, with more than 27·0 per cent. nickel, the resistance rapidly increases up to 30 per cent. of nickel, but is slightly lowered by hardening.

In the case of the second series, Table LIII., which contains medium percentages of carbon, the resistivity varies in the same manner as those just described, with the exception that the ranges of composition are different thus—

Nickel per cent.	Structure.
0·0 to 7·0.	Ferrite + pearlite.
7·0 to 26·0.	Martensitic.
Over 26.	Austenitic.

---

[1] *Journ. Iron and Steel Inst. Carnegie Memoir*, No. 1, 1909.

For the high carbon steels the same characteristic features are observed as for those just considered, but the limiting ranges for nickel are—

Nickel per cent.	Structure.
0·0 to 5·0.	Ferrite + pearlite.
5·0 to 15·0	Martensitic.
15·0 and over.	Austenitic.

Benedicks' formula only applies when the nickel content is less than 2·0 per cent.

TABLE LIII.—Electrical Resistance in Microhms per cm^3.

Carbon.	Nickel.	Silicon.	Manganese.	Normal Steels.	Hardened Steels.
0·07	2·23	0·070	0·025	16·6	20·0
0·12	5·23	0·046	0·015	22·2	22·4
0·12	7·13	0·050	0·050	24·9	25·8
0·13	10·10	0·100	traces	28·7	28·6
0·12	12·07	0·090	"	30·1	30·1
0·11	15·17	0·020	"	32·8	32·5
0·18	20·40	0·025	"	33·5	33·3
0·16	25·85	0·036	"	40·3	37·8
0·12	30·00	0·031	"	82·4	82·4
0·21	1·97	0·030	0·025	17·7	19·3
0·20	4·90	0·043	0·025	23·7	24·9
0·23	7·59	0·081	0·050	25·4	27·8
0·21	9·79	0·015	0·025	32·0	32·0
0·22	12·29	0·014	0·025	34·9	35·0
0·22	20·01	0·052	0·020	44·7	43·1
0·23	25·06	traces	0·020	72·0	73·2
0·19	27·87	0·260	0·025	82·6	82·6
0·80	2·20	0·100	0·107	21·9	36·6
0·78	4·90	0·085	0·092	31·4	46·2
0·81	7·09	0·100	0·125	37·0	50·2
1·05	9·79	traces	0·097	40·2	51·7
0·76	12·27	0·086	0·092	49·0	55·2
0·80	15·04	0·091	0·060	71·0	70·6
0·80	20·01	0·089	0·020	74·8	70·8
0·79	25·06	traces	0·070	80·4	79·1
0·81	29·96	0·139	0·030	85·4	85·4

Chromium Steels.—Two series of steels were investigated, the first containing about ·20 per cent. of carbon, and the second 0·8 per cent. The results are given in Table LIV. The hardened samples were heated to 980°, maintained at that temperature for five minutes and quenched in water at 12° C. It is somewhat misleading to compare these steels with microstructure in the same way as the nickel series, simply because in the case of chromium steels the microstructures depend so much upon the temperature to which they are heated, and the rate at which they are afterwards cooled.

In the low carbon series it will be seen that the electrical resistance increases more or less steadily with the percentage of chromium up to about 15 per cent., there is then a fall in the resistance as the chromium is raised to about 20 per cent., which is followed by another slight increase. The hardened samples give about the same values as the untreated ones, until there is 10 per cent. of chromium present, after which the former show a higher resistance than the latter. The maximum difference in this respect is manifest at approximately 15 per cent. of chromium.

With the high carbon steels, the untreated specimens show an increased resistance until 14 per cent. of chromium is present, after which it practically remains constant.

Hardening produces a marked increase in the resistance with steels containing up to approximately 15 per cent. Cr, but with higher percentages the values tend to become the same.

TABLE LIV.—ELECTRICAL RESISTANCE IN MICROHMS PER CM^3.

Carbon.	Chromium.	Silicon.	Manganese.	Untreated Steels.	Hardened Steels.
0·06	1·20	0·700	trace	16·3	18·0
0·28	2·66	0·050	0·150	29·7	31·0
0·21	4·50	0·232	trace	33·2	35·0
0·07	7·84	0·120	„	50·9	53·0
0·15	10·14	0·200	„	49·7	50·8
0·17	13·36	0·270	„	60·0	66·6
0·38	14·52	0·469	„	62·9	69·7
0·15	16·71	?	?	64·7	68·1
0·21	20·06	?	?	56·0	57·7
0·24	25·31	0·256	0·108	57·5	60·2
0·46	31·75	0·373	trace	63·7	66·3
0·86	0·62	0·243	0·027	23·1	43·5
0·97	0·99	0·221	0·244	25·8	50·2
0·89	2·14	0·280	0·108	27·8	54·0
0·79	4·57	0·420	trace	29·4	56·3
0·84	7·28	0·409	0·056	39·1	62·2
0·75	9·38	0·885	trace	56·4	66·5
0·70	13·94	0·180	0·240	65·4	72·5
0·74	14·54	0·486	trace	66·2	73·1
0·90	18·65	0·745	„	60·7	68·3
0·82	26·54	0·584	„	67·1	68·4
0·92	32·46	0·469	„	66·3	67·5
0·83	36·34	0·326	„	65·1	68·5
0·80	40·03	?	„	71·5	73·5

Tungsten Steels.—Portevin has determined the electrical resistances of a low and high carbon series of steels with varying tungsten content in the untreated and quenched condition, Tables LIV. and LV., whilst Swinden has made similar observation for a series in which the tungsten was constant at 3·0 per cent., with the carbon varying from 0·14 to 1·07 per cent., Table LVI.

For the low carbon steels it will be seen that the resistance increases with the tungsten until about 7·0 per cent. of that element is present, and then remains almost constant up to 26·0 per cent. of tungsten.

The resistivities of the quenched steels are practically the same as the untreated samples until more than 7·0 per cent. of tungsten is present, when the quenching produces a small increase.

With the high carbon alloys the quenched specimens, containing up to 10·0 per cent. of tungsten, give a considerably higher resistance than the untreated samples, but the difference in this respect becomes less as the tungsten is further increased.

TABLE LV.—Electrical Resistance in Microhms per cm^3.

Carbon.	Tungsten.	Silicon.	Manganese.	Untreated Steels.	Hardened Steels.
0·12	0·41	0·035	traces	12·8	13·8
0·11	0·93	0·058	,,	13·5	14·3
0·11	1·75	0·036	,,	15·8	17·1
0·13	4·96	0·035	,,	19·5	21·1
0·13	6·90	0·030	,,	23·3	23·4
0·17	11·89	0·046	0·067	20·9	24·5
0·20	14·37	0·060	traces	22·6	24·6
0·22	20·71	0·139	,,	23·1	25·3
0·22	24·35	0·112	,,	25·3	25·2
0·28	27·05	0·139	,,	20·7	25·8
0·86	0·40	0·040	0·027	22·4	39·1
0·66	0·95	0·120	0·054	20·9	39·6
0·79	2·75	0·058	0·054	24·3	40·9
0·33	4·68	0·140	traces	28·1	41·2
0·81	9·99	0·093	,,	26·9	39·5
0·71	14·75	0·117	,,	26·5	32·3
0·74	19·25	0·006	,,	25·3	31·0

TABLE LVI.—Dr. Swinden's Results.

Carbon.	Tungsten.	Silicon.	Manganese.	Untreated Steels.	Hardened Steels.
·144	3·25	·044	·065	17·3	19·24
·218	3·24	·050	·071	17·5	19·33
·27	2·92	·027	·170	17·6	20·20
·48	3·11	·060	·075	18·87	23·87
·53	3·18	·033	·140	18·4	25·64
·57	3·17	·078	·080	18·6	26·68
·89	3·08	·039	·093	17·6	36·6
1·07	3·09	·040	·055	17·0	38·7

NAME INDEX.

Abel—
  Separation of carbide of iron, 37.
Andrew—
  Action of caustic soda on mild steel, 140.
  Theory of hardening, 178.
Andrews—
  Structure of iron, 30.
Arnold, J. O.—
  On the Ar_2 and Ar_2 changes in iron, 25.
  Separation of carbide of iron from steel, 37.
  Constitution of martensite, 65.
  Troostite, 76.
  Effect of carbon on the mechanical properties of steel, 95.
  Strength and structure of pearlite, 101.
  Sulphur in steel, 110, 113.
  Theory of hardening steel, 164.
  Carbides in special steels, 193.
  Nickel-iron alloys, 194.
  Nickel-iron-carbon steels, 199.
  Tungsten steels, 209.
  Chemical constitution of manganese steel, 227.
  Chemical constitution of chromium steel, 234.
  Vanadium steel, 248.

Baker—
  Silicon steels, 246.
Barnes and M'William—
  Ultimate stress and Brinell hardness, 158.
Barrett—
  Molecular changes in iron, 23.
  Resistivity of steels, 261.
Bauer—
  Sulphide enclosures, 111.
Bedson—
  Wire-drawing, 134.
Beilby—
  Deformation and strain-hardening, 125.
Benedicks—
  On Ar_2 change in iron, 25.
  Constitution of iron-carbon alloys, 43.
  "Ferronite," 53.
Benedicks—
  Constitution of martensite, 65.
  Constitution of austenite, 73.
  Electric resistivity and specific volume, 75.
  Brinell test, 145.
  Rate of cooling, 180.
  Resistivity of iron, 260.
  Formula for resistivity of steel, 265.
Bessemer—
  Nickel steel, 194.
Böhler—
  Tungsten steel, 209.
  High-speed steel, 213.
Bottone—
  Atomic volume and hardness of metals, 161.
Boudard—
  Electrical resistance, 29.
Boynton—
  Troostite, 76, 78.
Bragg—
  Atoms in the molecule, 161.
Brinell—
  Soundness of steel ingots, 86.
  Sulphur in steel, 110.
  Hardness test, 145.
Brown—
  Resistivity of steels, 261.
Brunton—
  Heat-treatment of wire, 131.
  Wire-drawing, 134.
Burgess and Kellberg—
  Resistivity of iron up to 950° C., 261.

Campbell—
  Carbide of iron, Fe_2C, 58.
  Chemical composition and strength o steel, 100.
  Quenching temperature and resistivity 267.
Carnot—
  Chromium carbides, 234.
Caron—
  Separation of carbide of iron, 37.

Carpenter, H. C. H.—
  On the Ar_2 change in iron, 25.
  Recrystallising of electrolytic iron, 32.
  Freezing point of iron, 36.
  Thermal transformations in iron-carbon alloys, 39.
  Constitution of austenite and martensite, 72.
  Hardening of metals, 127.
  Theory of hardening steel, 176.
  Tungsten steels, 209.
  High-speed cutting steel, 219.
  Chromium steel, 237.
  Aluminium bronze, 246.
Cartaud—
  Crystalline character of iron, 33.
Caspersson—
  Position of blowholes in ingots, 86.
Chappell—
  Recrystallisation of deformed iron, 128, 131.
Charpy—
  Dilatation, 29.
  Constitution of iron-carbon system, 43.
  Constitution of martensite, 73.
  Recrystallisation after deformation, 131.
Cheever—
  Phosphorus, 104.
Curie—
  Magnetic properties, 26.

Dumas—
  Nickel steels, 201.

Edwards—
  Microstructure of steel, 70.
  Crystal twinning by quenching, 72.
  Austenite and martensite, 74.
  Hardening of metals, 127.
  Theory of hardening, 176.
  Twinning of crystals, 172.
  Tungsten steels, 209.
  High-speed steels, 219.
  Chromium steels, 237
  Copper-aluminium bronzes, 246.
Edwards, Greenwood, and Kikkawa—
  Influence of initial temperature on chromium steels, 240.
Ewen—
  Intercrystalline cohesion of metals, 17.
Ewing—
  Twinning and slip bands, 20.
  Deformation and strain-hardening, 125.

Foëx—
  Magnetic properties, 27.
Fournel—
  Electrical resistivity, 261.
Fuchs—
  Crystalline structure of iron, 30.

Giesen—
  Vanadium carbide, 249.
Gilbert—
  Effect of temperature on the properties of iron and steel, 23.
Gledhill—
  High-speed steel, 213.
Goerens—
  Influence of cold work and annealing on iron and steel, 131, 135.
Gore—
  Internal changes in iron, 23.
Goutal—
  Chromium carbides, 234.
Grenet—
  Dilatation, 29, 73, 75.
  Theory of hardening steel, 170.
  Depth of penetration of quenching effect, 190.
Guertler—
  Resistivity and constitution, 264.
Guillaume—
  Nickel steels, 196.
Guillet—
  Case-hardening, 141, 144.
  Nickel steel, 201.
  Tungsten steel, 209.
  Aluminium and silicon steels, 210.
  Manganese steel, 231.
  Chromium steel, 244.
  Vanadium steels, 246.
Gutowsky—
  Solidus of iron-carbon system, 39, 43.

Hadfield, Sir Robert—
  Molecular formula of carbide of iron, 37.
  Method of producing sound ingots, 90.
  Hardness and other physical properties, 159.
  Theory of hardening steels, 166.
  Nickel-iron alloys, 197.
  Tungsten-carbon steels, 209.
  Manganese steels, 231.
  Chromium steels, 234.
  Aluminium steels, 246.
  Resistivity of steels, 261.
Harker—
  Specific heats of iron, 29.
Hatfield—
  Ultimate stress and Brinell hardness 158.
Heyn—
  Sulphide enclosures, 111.
  Rapid recrystallisation of iron, 131.
Hopkinson—
  Magnetic properties of nickel steel, 194.
  Resistivity of steel, 260.

HOWE—
Piping in steel ingots, 9.
Burning and overheating, 117.
HOWE and LEVY—
Rates of cooling and carbon steels, 180.
HUMFREY—
Structure and properties of iron at high temperatures, 34.
Theory of hardening, 177.

JOHNSON—
Resistivity of steels, 261.
JUPTNER—
Phosphorus, 104.
Molecular condition of carbon in steel, 266.

KARSTEN—
Carbide of iron, 36.
KEELING—
Thermal changes in iron-carbon alloys, 39, 42.
KENNEDY—
Carbide of iron, 58.
KIKKAWA—
Chromium steels, 237.
KIRSCH—
Nickel steels, 196.
KOURBATOFF—
Constitution of troostite, 76.

LAW—
Sulphides in steel, 113.
LE CHATELIER—
Constitution of iron-carbide alloys, 43.
Martensite, 64.
Austenite, 73.
Volume change at Ar_1, 75.
Troostite, 76.
Sulphur in steel, 113.
Rapid recrystallisation of iron and mild steel, 131.
High-speed cutting steel, 219.
LEDEBUR—
Separation of carbide of iron from steel, 37.
LONGMUIR, P.—
Wire-drawing, 131.
Acid cleaning of cold drawn wire, 135.
Corrosion of metals, 139.
LUDWIK—
Hardness testing, 149.
Hardness at elevated temperatures, 161.

M'CANCE—
Constitution of Troostite, 76.
Magnetic permeability, 78.
Theory of hardening steels, 178.
Molecular condition of carbon in steel, 268-270.
M'WILLIAM—
Strength and structure of pearlite, 101.
MARTELL—
Hardness testing, 153.
Law of volume of indent and energy of blow in dynamic hardness test, 153.
MATHEWS—
Electrical resistivity, 261.
MATTHIESSEN—
Electrical resistivity, 261.
MATWEIEFF—
Manganese and ferrous sulphides, 113.
METCALF—
Theory of hardening, 166.
MORRIS—
Magnetic properties of iron, 27.
MÜLLER—
Separation of carbide of iron, 37.
MURAKAMI—
Chromium-iron-carbon alloys, 241.

OSMOND, F.—
Transformation in iron and iron-carbon steels, 23.
Interpretation of Ar_2 change in iron, 24.
Crystalline character of iron, 33.
Effect of carbon upon thermal changes in iron, 37.
Constitution of iron-carbon system, 39.
Constitution of martensite and austenite, 64.
Austenite, 73.
Troostite, 76.
Theory of hardening steel, 164.
Amorphous phase, 172.
Effect of special elements on steel, 193.
Iron-nickel alloys, 196.
Nickel-iron-carbon steels, 200.
Tungsten-carbon steels, 209.
High-speed-cutting steels, 219.
Chromium steel, 234.

PERCY—
Crystalline structure of iron, 30.
Phosphorus, 104.
PORTEVIN—
Electrical resistivity, 261, 265.
PREESE—
Resistivity of iron, 260.
PUTZ—
Vanadium carbide, 249.

READ—
Separation of carbides of iron from carbon steel, 37.
Carbides in special steels, 193.
Tungsten steels, 209.
Manganese steels, 229.
Chromium steels, 235.
Vanadium steels, 249.

RICHARDS—
  Physical properties of elements as periodic functions of their atomic weights, 161.
RILEY—
  Nickel-iron alloys, 194.
RINMAN—
  Carbide of iron, 37.
ROBIN—
  Rapid growth of ferrite on annealing after deformation, 131.
ROBERTS-AUSTEN—
  Cooling curve of iron, 24.
  Constitution of iron-carbon alloys, 37.
  Troostite, 76.
  Theory of hardening, 166.
RÖHL—
  Sulphides, 113.
ROOZEBOOM—
  Constitution of iron-carbon system, 39.
ROSENHAIN, W.—
  Intercrystalline cohesion of metals, 17.
  Slip bands, 20.
  Structure and strength of iron at high temperatures, 34.
  Sulphur in steel, 113.
  Deformation and strain-hardening, 125.
  Amorphous state in metals, 127.
RUER—
  Constitution of iron-carbon system, 43.

SAKLATWALLA—
  Constitution of iron-phosphorus alloys, 104.
SALDAU—
  Electrical resistivity, 261.
SANDBURG—
  Sorbitic steel, 184.
SANITER—
  Structure of iron at high temperatures, 33.
SAVEUR—
  Growth of ferrite below its thermal critical point, 131.
SCHNEIDER—
  Iron-phosphorus, 104.
SHAW-SCOTT—
  Cementation of iron, 141
SNELUS—
  Segregation, 84.
STANSFIELD—
  Overheating and burning, 117.
STEAD, J. E.—
  Recrystallising of iron, 24.
  Internal structure of iron, 31.
  Electrolytic iron, 32.
  Intercrystalline segregation, 84.
  Blowhole segregation, 88.
  Phosphorus and iron, 104.
  Sulphur in steel, 115.
  Overheating and burning of steel, 118.
  Rapid recrystallisation of iron and mild steel, 131.
  Manganese carbide, 229.
  Electrical resistivity, 261.
STROMEYER—
  Ageing of mild steel, 140.
STROUHAL—
  Electrical resistivity, 261.
STUBBS—
  Segregation, 84.
SWINDEN—
  Tungsten steels, 209.
  High-speed cutting steels, 221.
  Electrical resistivity, 261.

TAMMANN—
  Hardening of metals, 126.
TALBOT—
  Solidification of steel, 85, 94.
TAYLOR—
  High-speed cutting steels, 214, 218.
TCHERNOFF—
  Critical points and hardening of steel, 23.
THOMPSON—
  Transport of electricity through metals, 259.
TROOST—
  Troostite, 76.
TURNER—
  Silicon steels, 246.

UPTON—
  Constitution of iron-carbide alloys, 42.

WAHLBERG—
  See Brinell, 86.
WATERHOUSE—
  Nickel steels, 199.
WEISS—
  Magnetic properties, 27.
WERTH—
  Separation of carbide of iron, 37.

INDEX TO SUBJECTS.

A

Acid cleaning of steel, 139.
Allotropy, 1.
Allotropic changes in iron, 23.
—— —— —— metals, 1, 7.
Alloys, Constituents in, 3.
—— freezing point diagrams of binary systems, 5.
—— —— —— —— —— ternary systems, 9.
—— thermal critical points and ranges, 3.
Alpha iron, 25.
Aluminium, Effect of, on soundness of steel ingots, 88.
—— steel, 246.
Amorphous phase in metals, 17.
—— —— on polished surface of metals, 15.
—— —— produced by deformation, 126.
—— —— —— —— quenching steels, 172, 176.
Annealed steels, Constituents in, 52.
Annealing, *see* Refining, 121.
Austenite, 62, 64.

B

Blowholes, 81, 88.
Brinell test, 145.
  Diameter of indent and hardness number, 150.
  Influence of load, 148.
  —— of time, 152.
  Relation between dynamic test and Brinell, 154.
  Ultimate stress and Brinell, 158.

C

Carbides in chromium steel, 234.
—— —— iron-carbon steels, 37.
—— —— manganese steels, 227.
—— —— nickel steels, 199.
—— —— tungsten steels, 209.
—— —— vanadium steels, 248.
Carbon, Graphitic, in steel, 95.
—— influence on properties of steel, 95.
Carbon-iron alloys, Constitution of, 36.
—— —— Critical points in, 36.
—— —— Equilibrium diagram of, 36-50.
Carbon-nickel steels, 199.
Carbon steels, Constitution of annealed, 52.
—— —— —— —— quenched, 61.
—— —— Mechanical properties of, 95.
—— —— Microstructure of, 51.
Case-hardening ordinary carbon steels, 141.
—— nickel steel, 143.
Cast steel, Refining of, 121-124.
Cementation, *see* Case-hardening.
Cementite, 57.
—— Decomposition of, 58.
—— Hardness of, 78.
Chromium, carbides, 234.
—— Effect of varying rates of cooling on carbide change, etc., 238-241.
—— Self-hardening of, 237.
—— steels, 234.
Chromium-tungsten steel, high-speed cutting tools, 214.
—— —— Microstructure of, 221.
—— —— Tempering of, 216.
Cold drawn wire, 134.
Cooling curves, 39.
Critical points in iron, 23 (Ar_3, Ar_2), 37.
—— —— in carbon steel, 37.
—— —— Effect of rapid cooling upon the temperature of, 170, 180.

D

Definition of constituents in steel, 51-78.
Deformation of metals, 125.
—— —— slip bands, 126.
—— —— twin crystals, 130.
Dynamic test—
  Indentation and Brinell number, 154.
  —— and elastic rebound, 157.
  Martell's law, 153.

E

Electrical resistance and constitution, 259-272.
  Influence of other elements on resistivity of iron, 265.
  —— of quenching temperature on resistivity of carbon steels, 262-267.
  Resistivity of iron, 260, 265.
Electrolytic iron, Rapid recrystallisation of, 32.
Etching, 15.
Eutectics, 3.
Eutectoids, 3.
—— iron-carbon eutectoid, 44-47, 59.

F

Ferrite, 52.
—— Hardness of, 78.
Fineness of structure, effect on properties of metals, 170.

H

Hardening of steel, theories, 164.
—— —— —— Allotropic theory of, 164, 169.
—— —— —— amorphous phase, 172, 175.
—— —— —— crystal twinning, 172, 176.
—— —— —— Lowering of Ar_1 change, 170, 238.
—— —— —— suppression of Ar_1 change, 170, 176, 238.
Hardness and molecular attraction, 160.
—— and other physical properties, 162.
—— of micro-constituents of steel, 78.
—— testing, 145-163.
Heat, Specific, of iron, 29
Heating, prolonged, Influence of, *see* Overheating.
Heat-treatment, burning and overheating of steel, 117-124.
—— high-speed cutting tools, 213-217.
High-speed tool steel, 213.
—— —— —— Composition of, 214.
—— —— —— Cutting powers of, 218.
—— —— —— effect of initial temperature upon carbide change, 219.
—— —— —— hardness of annealed and hardened, 217.
—— —— —— high-heat-treatment of, 215.
—— —— —— Influence of tempering on, 215.
—— —— —— microstructures, 221.
—— —— —— secondary treatment, 215.
—— —— —— red-hardness, 215.
—— —— —— Vanadium in, 218.
Hydrogen, Absorption of, during acid cleaning of steel, 139.
—— —— —— by action of caustic soda, 140.
—— Effect of, on critical point of iron, 25.
—— Influence of, on crystallisation of steel, 140.

I

Ingots, aluminium, manganese, and silicon, Influence of, 87.
—— blowholes, 86.
—— Blowhole segregation in, 88.
—— composition and soundness, 86.
—— Fluid compression of, 91.
—— gases, Effect of, during solidification, 80.
—— intercrystalline segregation, 84.
Ingots, Piping in, 81.
—— position of pipe and blowholes, 86.
—— segregation in steel, 84.
—— solidification of steel, 79.
Initial temperature and rate of cooling, 179-190.
  Carbon steels, 180.
  Chromium-carbon steels, 237-242.
  Nickel-chromium steels, 187.
  Other special steels, 187-192.
Iron, 23.
—— Allotropic forms of, 23-26.
—— Cementation of, *see* Case-hardening.
—— Critical points in, 23-26.
—— Dilatation of, 28.
—— Electrical resistance of, 29.
—— Freezing point of, 36.
—— Magnetic properties of, 26.
—— Rapid recrystallisation of, 31-34, 131.
—— Strength of, at high temperatures, 34.
Iron-carbide, 37.
Iron-carbon alloys, *see* Carbon-iron alloys.
Iron-phosphides, 104.
Iron-sulphide, 110.

L

Ludwik test, 149.

M

Magnetic properties of iron, 26.
Manganese, Carbide, 229.
—— Sulphide, 110.
Manganese steels, 227.
—— —— Critical points in, 229.
—— —— Mechanical properties of, 231.
Martensite, constitution, 62.
—— Hardness of, 78.
Melting point, diagrams of alloys, 5-14.
—— —— diagram of iron-carbon system, 39.

Melting point of iron, 36.
—— —— of metals, 3.
Microstructure of annealed steels, 52-61.
—— —— high-speed steels, 188.
—— —— iron, 29.
—— —— metals, 15-22.
—— —— quenched steels, 61-78.
Moulds, effect of size upon position of blowholes and pipes in ingots, 88.

N

Nickel-iron alloys, influence of nickel on critical points, 195.
—— —— magnetic properties, 194.
—— —— mechanical properties, 196-198.
—— —— reversible and irreversible alloys, 195.
Nickel-iron-carbon steels, Heat-treatment of, 196.
—— —— Mechanical properties of, 199-208.
Nitrogen in case-hardening, 142.

O

Overheating of steel, effect on structure and properties, 121.
—— —— —— refining of overheated steel, 121.
Oxides reduced by manganese, 227.

P

Pearlite, constitution, 59.
—— Coarsening of, 60.
—— Sorbitic, 61.
Phase rule, 2, 165.
Phosphorus, Effect of carbon, on solubility in iron, 106.
—— Effect of, on rate of crystal growth in steel, 109.
—— —— —— on temperature of critical points, 109.
—— equilibrium diagram of iron-phosphorus system, 105.
—— iron-phosphorus compounds, 104.
—— Segregation of, in blowholes, 88.
Pickling of iron and steel, *see* Acid cleaning.
Piping in steel ingots, 80.

Q

Quenched steel, Constitution of, 61.
—— —— Specific volume of, as compared with annealed, 75.
Quenching, effect on critical points, 62, 237.
—— Theory of, 62, 65.
—— Twinning of crystals produced by, 70.

R

Recalescence curves of iron, 23, 26.
—— —— —— chromium steel, 237.
—— —— —— high-speed steels, 220.
—— iron-carbon steels, 40.
Red-shortness caused by sulphur, 110.
—— —— —— blowhole segregation of sulphur, 90.
Refining of steel castings, 121.
—— —— —— overheated steel, 121.
Ropes, Deterioration of, 139.

S

Segregation, 84.
—— blowhole segregation, 88.
Shore scleroscope, 152-157.
Silicon, Effect of, on soundness of steel ingots, 88.
—— steels, 246.
Slip bands, or lines, 125.
Solid solutions, 3.
Sorbitic pearlite, 61.
Special steels, 179.
Strain-hardening, 125.
Sulphur, Manganese and iron, 110, 115.
—— prints, 113.

T

Tempering of high-speed steels, 216.
Tool steel, *see* High-speed.
Troostite, 76.
Tungsten steels, 209.
—— —— Constitution of, 210.
Twin-crystals, 17.
—— produced by mechanical strain, 131.
—— —— —— quenching, 70.

V

Vanadium in high-speed steel, 214.
—— carbides, 250.
—— steel, 248.

W

Wire, Acid cleaning of, 134, 139.
—— Cold-drawn, 134.
—— Galvanising, 138.
—— removal of hardness caused by cold work, 138.

BELL AND BAIN, LIMITED, PRINTERS, GLASGOW.